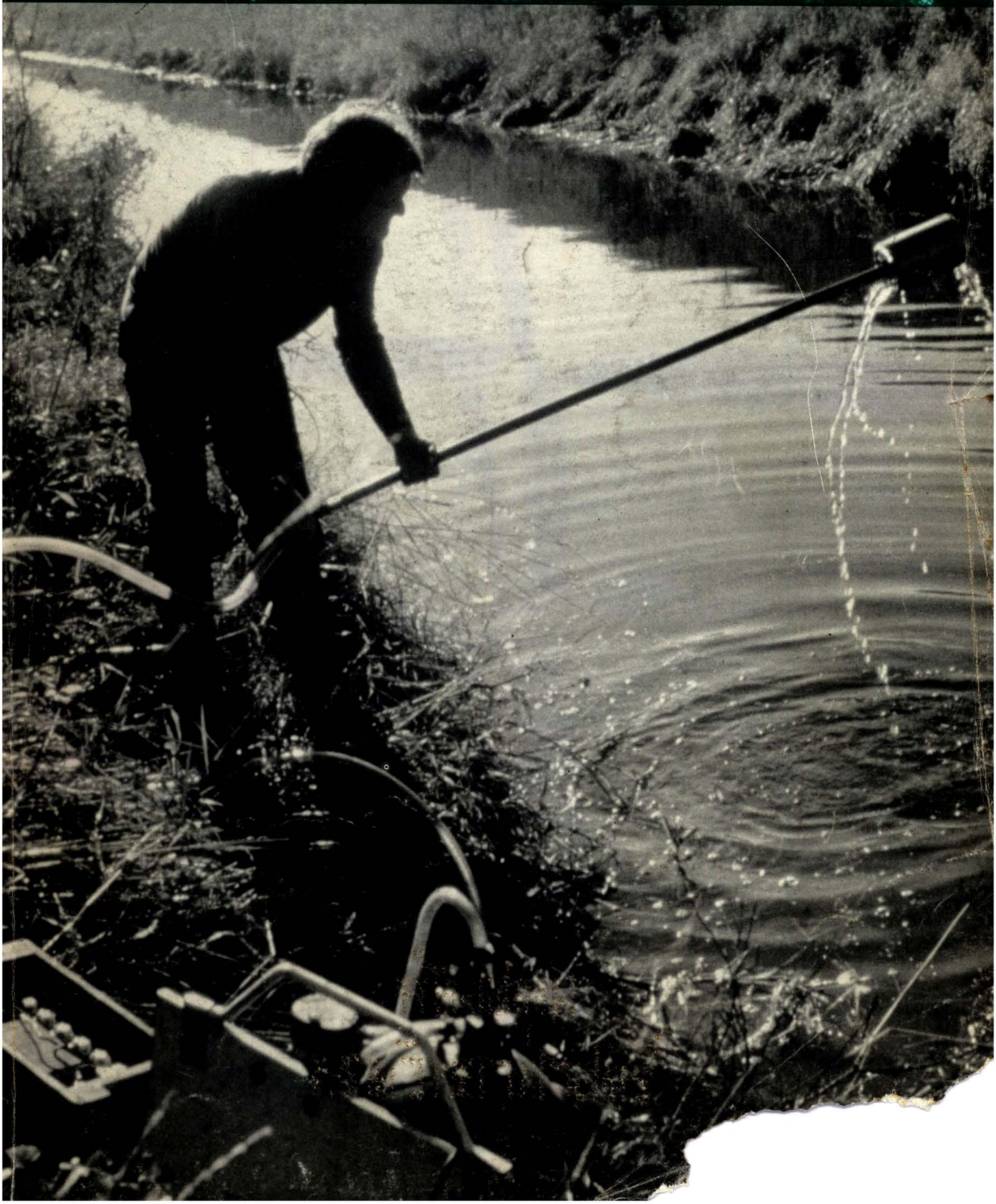
FEBRUARY 1987

# ENVIRONMENTAL PROGRESS



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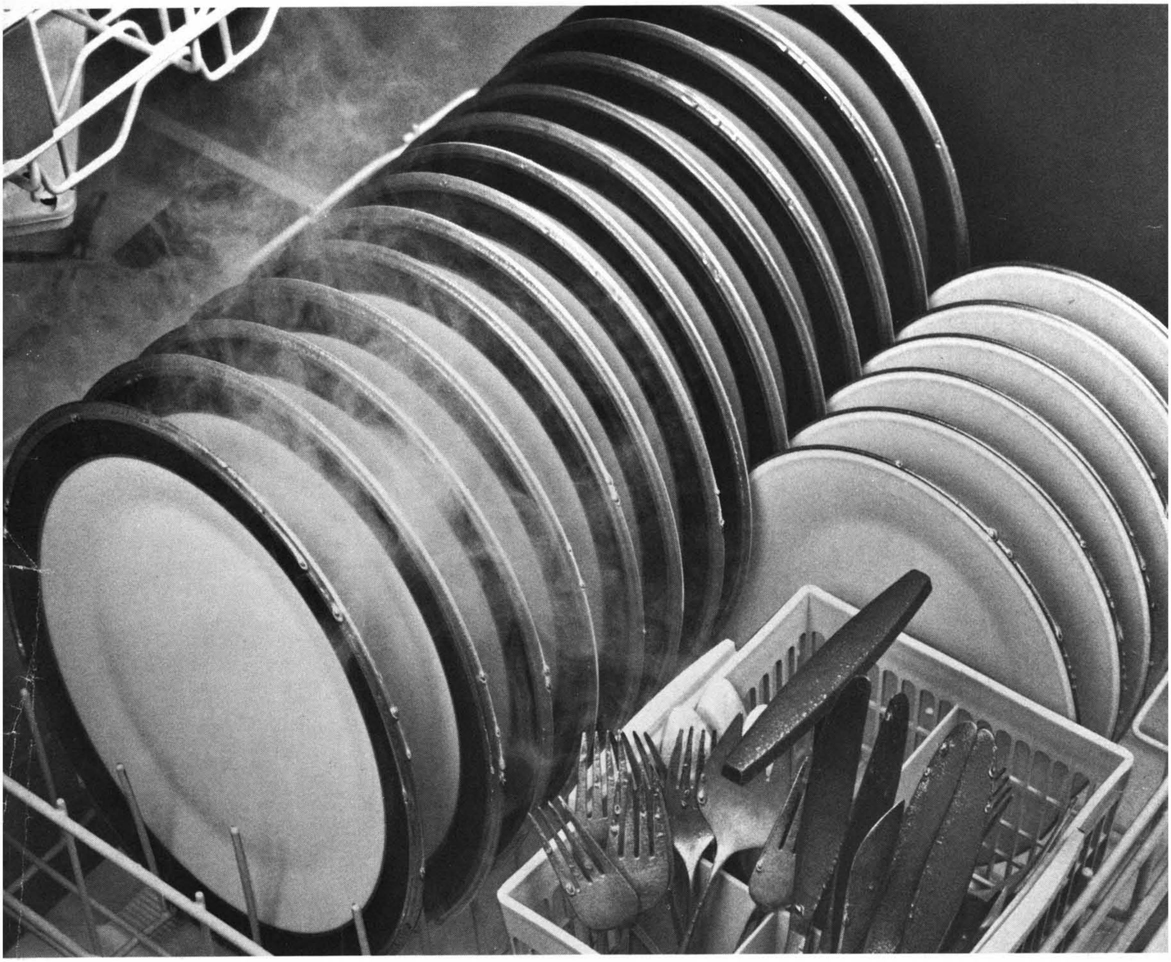

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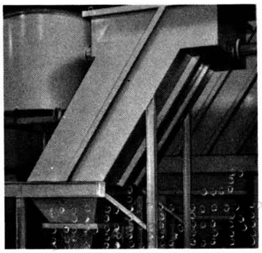

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# ENVIRONMENTAL PROGRESS

**Environmental Progress is a publication of the American Institute of Chemical Engineers. It will deal with multi-faceted aspects of the pollution problem. It will provide thorough coverage of abatement, control, and containment of effluents and emissions within compliance standards. Papers will cover all aspects including water, air, liquid and solid wastes. Progress and technological advances vital to the environmental engineer will be reported.**

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Volume 6

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Number 1

**Cover: A sample being taken from a waterway to study the effects of a herbicide. Photo courtesy of Monsanto Company, St. Louis, MO.**

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## JOURNAL OF HAZARDOUS MATERIALS

**Management-Handling-Disposal-Risk Assessment**

**Editors:**
G.F. Bennett, University of Toledo, Toledo, OH, USA
R.E. Britter, Cambridge, UK
Regional Editor for Japan:
Y. Uehara, Japan Society for Safety Engineering, Yokohama, Japan

The journal brings together original papers covering all the environmental problems that can arise from the manufacture, use and disposal of potentially hazardous materials. Particular attention is paid to procedures thatminimise risks, including the safe design of plant, its effective maintenance, transport standards, and detoxification or neutralisation of residues and wastes.

Relevant legislation, both national and international, is reviewed, with indications of trends and cooperative ventures. Standards, codes of practice and safe levels for workers and the general population are included as they are specified. Means of preventing incidents involving hazardous materials are considered in detail, illustrated where possible by case histories from which general lessons can be learned. Preferred methods of dealing with incidents of all types, hazard labelling and sources of information and advice are also included.

Subscription Information
1986: Vols. 13 & 14 (6 issues)
US$ 192.50 / Dfl. 558.00
1987: Vols. 15 & 16 (6 issues)
US$ 236.00 / Dfl. 590.00

***Free sample copies are available on request***

## JOURNAL OF OCCUPATIONAL ACCIDENTS

**Editor:**
H.S. Eisner, Buxton, UK

Since 1976 the Journal of Occupational Accidents (JOCA) has served as an international medium for the publication of research in the science and technology of accidents at work. It gathers under one cover accounts of researches that previously had to find their way into journals of many disciplines and countries, much to the detriment of ease of retrieval.

JOCA scans the variegated panorama of occupational safety, as distinct from health, the dividing line being drawn generously. It concentrates on the why and how of the accident as an event and on the many opportunities at all stages for preventive or palliative action. It does this by relating its approach to specific hazards rather than industries, except when an industry such as mining or forestry presents special risks.

Like safety itself, JOCA is multidisciplinary. Its contributors are as likely to be industrial psychologists as chemical engineers, their method analytical, experimental or both. While JOCA is in the forefront of research, it welcomes the occasional state-of-the-art review as well as first-hand case histories of accidents and disasters of special significance and statistical surveys of accident experience throughout the world.

Subscription Information
1986: Vol. 8 (4 issues)
US$ 80.75 / Dfl. 234.00
1987: Vol. 9 (4 issues)
US$ 100.00 / Dfl. 250.00

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# Truth or Consequences

### Gary F. Bennett

Having been engaged by the attorneys for the plaintiff in a citizen's law suit against a local foundry, I learned the opposing attorney was a close personal friend. He paid me the honor of commenting that he wished I were on his side and not the other "but at least I know you are honest" he said. I was baffled by his remark for I have never considered any other course of action than being honest. For instance, I would never go out of my way to volunteer information helpful to the other side nor would I undertake research to assist their claim. Nevertheless, if asked a question, the correct answer to which was beneficial to the opposition, I would answer truthfully and accurately.

When I expressed my puzzlement to my friend he said "believe it or not, not all expert witnesses are honest and lawyers can get experts to take virtually any point of view they want". Unconvinced, I put the same question to an attorney who presented a paper at a recent AIChE meeting. After a long pause the attorney quietly and reluctantly confirmed what my friend had said.

It is saddening to learn that there are people in our profession who will deliberately misinterpret the facts in a court of law. The implication for both attorneys was that opinions can be bought and engineers brought in to support almost any point of view whether the engineer in question believes in that viewpoint or not. As far as I am concerned this kind of behavior is entirely unprofessional.

It has also been suggested that, rather than finding scientists who will expound their own point of view, lawyers shop for scientists who have expressed and believe in the interpretation favorable to their client's side. I do not believe the scientist is being dishonest in this situation.

I have no problem with scientific disagreement, and in the environmental areas we have many, such as, need for control of acid rain, to ban or not to ban phosphates in soap, proper discharge limits for certain materials, etc. These are issues on which very good, and honorable scientists have differing opinions, many of which are based on differing interpretations of the same data. These are respectable, honest, differing points of view, and I respect my colleagues who differ from me in this way. This respect would fade, however, if I felt these points of view were based on shoddy, incomplete analysis and it would totally dissolve if I felt my colleagues took a point of view in complete revocation of all the evidence, plus their personal beliefs, to the contrary.

My editorial is based on limited experience in the field of scientific law. I would be interested in hearing of the reader's experience along these lines or of any reactions to my comments.

---

**Gary F. Bennett** *has been editor of* Environmental Progress *since its inception in 1982. Active in AIChE, he is a tour speaker, past chairman of the Environmental Division and recipient of two National awards—Service to Society and the Environmental Division Award. He is currently Professor of Biochemical Engineering at the University of Toledo.*

# Environmental Shorts

## Municipal Wastewater Treatment System In Texas To Expand Under Modified Privatization Arrangement

Air Products and Chemicals, Inc., has been selected to expand the wastewater treatment system of the City of Kerrville, Texas, under a modified privatization arrangement. Air Products will incorporate its proprietary A/O® wastewater treatment system in the expansion, and will manage all phases of the design, engineering and construction of the project. In addition, Air Products will provide operator training and will supply technical service and operating assistance for the expanded plant under a multi-year contract.

At Kerrville, Air Products will upgrade the city's existing oxidation ditch process to the A/O wastewater treatment process, a highly energy-efficient biological system which will remove BOD, nitrogen and phosphorus from its municipal wastewater. The conversion will significantly increase the capacity of Kerrville's wastewater system at a considerably lower capital cost than standard treatment systems. The expanded system is expected to be operational by the end of 1987.

## Shortage of Hazardous Waste Treatment and Disposal Capacity Expected

A recent ICF Incorporated survey of 17 major commercial hazardous waste management firms indicates that hazardous waste generators expect such a serious shortage of waste treatment and disposal capacity by the end of the decade that they have begun to buy up incineration time and landfill space through 1987 and beyond. In addition, more and more generators are talking to commercial waste management firms about building and operating treatment and disposal units at the generators's facility and, in some cases, allowing commercial use of the units.

"Commercial waste management firms, especially those with incinerators report that customers without such 'reservations' are likely to face longer and longer waiting periods," said ICH's Geoff Back, who summarized the survey findings in the new report, "1985 Survey of Selected Firms in the Commercial Hazardous Waste Management Industry".

# LETTER

## On "A Mathematical Model of Settling Velocity Enhancement by Kinetic Control" by Karl B. Schnelle, Jr., Karl D. Schnelle, Steve J. Gibbs and David J. Wilson

*Environmental Progress* 4, 259 (1985)

**To the editor:**

The authors presented a model of the sedimentation behavior of suspensions in upflow clarifiers or reactor-clarifiers [*1*]. The resulting suggestion that the settling of chemical precipitates can be enhanced is of appreciable importance and interest; the model on which the study was founded, however, is inappropriate.

The authors' Equation 2 is the basis of the analysis (note that the last term in the denominator should be preceded by a plus sign). It was obtained by (1) adopting Stokes' law [*2*] describing the subsidence velocity of a discrete particle in an infinite fluid, (2) substituting Fair and Geyer's empirical expression [*3*] for the coefficient of drag, $C_d$, in Stokes' equation as a function of Reynolds number, R,

$$\left(C_d = \frac{24}{R} + \frac{3}{\sqrt{R}} + 0.34\right)$$

and (3) replacing absolute fluid viscosity with an empirical expression (the authors' Equation 1) for the viscosity of a concentrated suspension of particles.

The resulting expression (the authors' Equation 2) describes the velocity at which a single particle settles through a suspension of particles. That is, the equation describes the rate a particle will settle when its downward motion is resisted by drag forces caused by flow of a suspension of particles. The suspension of particles is considered to be sufficiently concentrated to cause its viscosity to be greater than that of the suspending liquid. The appreciable effect of the concentration of particles on sedimentation velocity (as described, for example, by Richardson and Zaki [*4*]) is not considered in the analysis; instead, Stokesian sedimentation of discrete particles is tacitly assumed.

The conceptual and theoretical basis of the analysis are flawed. Particles in upflow or reactor clarifiers do not settle as discrete entities through a concentrated suspension of particles with altered viscosity. Instead, the mother liquid (ordinarily water) flows about particles. The fluid drag on particles is imparted by the liquid, not a suspension with viscosity increased by the presence of particles. Also, particles in reactor clarifiers do not settle (or remain stationary because of the upward flow of liquid) as discrete entities in a infinite fluid. Instead, the particle concentration in upflow settlers is so high that zone sedimentation occurs [*5*].

In effect, the authors substituted the influence of particle concentration on fluid viscosity for the effect of particle concentration on sedimentation velocity. They suggest Figure 4 demonstrates the validity of the approach, but the figure merely shows that Equation 2 with its two empirically determined variables is sufficiently flexible to accommodate the experimental data. No mechanistic conformance with the model can be inferred.

The authors concluded that the radius of chemical precipitates decreased with residence time in the mixer. This was deduced by using experimental results to solve for particle radius using Equation 2 (see the authors' Table 2). Because the equation does not describe the phenomena establishing the experimental results, the assumption that one of the empirical coefficients in Equation 2 represents particle radius is not warranted.

In summary, the authors analyzed performance of upflow clarifiers by assuming fluid drag on particles is related to the viscosity of a concentrated suspension and by ignoring the influence of particle concentration on sedimentation velocity. The suspending liquid, not the suspension, flows about particles, however, and its viscosity establishes fluid drag. The high concentration of particles in upflow clarifiers causes sedimentation velocities to be far lower than the Stokesian velocity of individual particles in the suspension. Because phenomena in upflow clarifiers differ from those included in the authors' analysis, caution is necessary in inferring settling velocity enhancement by kinetic control.

### Literature Cited

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3. Fair, G. M. and Geyer, G. C., *Water Supply and Waste-Water Disposal,* John Wiley and Sons, Inc., New York, (1954).
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5. Bond, A. W., *J. Sanit, Engrg. Div. Am. Soc. Civil Engr.*, **86,** SA3, 57 (1960).

**Richard I. Dick**
Joseph P. Ripley Professor
of Engineering
Cornell University
School of Civil and
Environmental Engineering
Ithaca, NY.

# INSTITUTE NEWS

## AIChE Announces Major Changes in Meeting Presentation Scheduling

### Changes Effective with 1987 Summer National Meeting in Minneapolis

AIChE Council, at its meeting of November 1, 1986 in Miami Beach, approved the recommendations of the Executive Board of the Program Committee (EBPC) and the Publication Committee, to change the scheduling requirements for proposals to present papers at AIChE meetings, submission of manuscripts, and related topics. Following is a description of the approved changes which are being incorporated in the scheduling of AIChE's 1987 Summer National Meeting in Minneapolis.

Speakers will have up to five additional months prior to a meeting to submit **Proposals To Present** to Session Chairmen. Proposals to Present must be received by Session Chairmen no later than six months prior to a meeting. A proposal may be submitted any time before that, once Session Chairmen have been identified (usually one to two years before a meeting) and announced in *CEP.* All Proposals to Present received at least six months prior to a meeting will be considered by Session Chairmen. Session Chairmen are asked not to make final selections until six months prior to the meeting.

Sixty word abstracts of accepted presentations will be eliminated from the Meeting Program Book. Instead, when a proposal is accepted for presentation (five months prior to the meeting), Session Chairmen will mail each speaker a revised Presentation Acceptance Form with room for each speaker to prepare a **one-page extended abstract** of his or her presentation. Speakers must return the completed, clearly typed Presentation Acceptance form, with abstract, to Session Chairmen at least ten weeks prior to the meeting. These abstracts will be collated by session, reproduced, and distributed free to meeting attendees upon registration at the meeting.

The **Meeting Program Book** will contain all the information it now contains except for the 60-word abstracts. It will be mailed to all members of the Institute on the same schedule as it is now - 10 weeks prior to the meeting.

Speakers will no longer be required to submit **manuscripts** to the AIChE Manuscript Center three months prior to the meeting date to meet the deadline for microfiche preparation. Speakers will be required to submit full manuscripts (four copies) to Session Chairmen one month before the meeting.

**Microfiche** of presentations will be prepared immediately after each meeting. This will allow preparation of better organized and more complete fiche. Microfiche will continue to be sold at each meeting and orders for a current meeting's microfiche can be placed at the Publication Sales Desk at the meeting, or through AIChE's other regular sales channels.

**A photocopying service** will be set up at each meeting to allow meeting attendees to purchase hard copies of full manuscripts. Meeting attendees will be able to order copies of manuscripts 24 hours or more in advance of a session or group of sessions. It is the responsibility of each Session Chairman to make sure that reproducible copies of all papers in the session are submitted to National Headquarters so that this service can be set up effectively. The length of the total manuscript (including copies of slides) should be kept under 40 typewritten pages.

AIChE will no longer ask authors to sign a **Transfer of Copyright** agreement at the time a paper is submitted for presentation. Only those authors whose papers are accepted for publication by AIChE will be asked to sign the Copyright Transfer. Authors will be notified when a paper is accepted for publication or is to be released.

To protect the author's copyright interests, each manuscript submitted to Session Chairmen, whether the author wishes it to be considered for publication or not, must have the following on the title (cover) page:

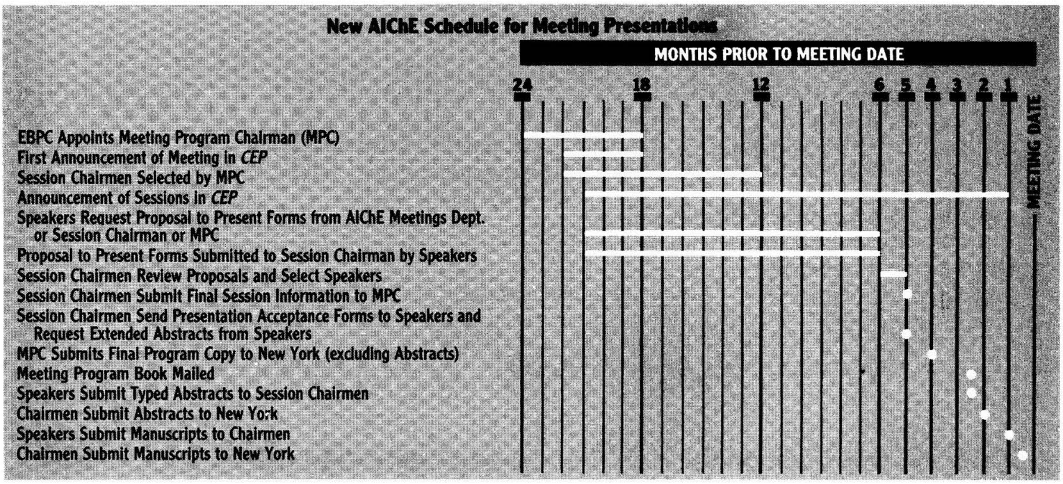
"Title
Author(s)
Affiliation
Prepared for presentation at [Meeting Name/Date, Session Name/ Session #]
Copyright© [Author(s) Name (or Employer for whom work was performed if Employer holds the copyright]
Date [Month/year]
UNPUBLISHED"

(Employees of the U.S. Government who prepared the work as part of their employment should omit the copyright statement.)

Effective with the Minneapolis Summer Meeting, speakers will be permitted to use **overhead projectors** during their presentations. Guidelines for preparation of overhead transparencies and the use of overhead projectors and other audio-visual equipment will be available shortly from AIChE's Meetings Department.

The table below shows the beginning and end dates of the activities described above. Anyone who wishes more information on the schedule changes, forms, or submission requirements and dates, should call or write to

**AIChE Meetings Department**
345 East 47th Street
New York, NY 10017
(212) 705-7325



Reprinted from *Chemical Engineering Progress* **83**, No 1, 80 (1987).

# Washington Environmental Newsletter

## Title III of SARA (Superfund Amendments & Reauthorization of 1986)

AIChE local sections that are already involved, or planning a program to assist communities with their Emergency Response Planning should be advised that Title III of the Superfund Amendments & Reauthorization Act of 1986, *requires* communities to put in place a hazardous materials emergency plan. The "Emergency Planning and Community Right-to-Know Act of 1986" replaces the voluntary participation of communities that was promulgated in early 1986 by the EPA. Title III of SARA requires the establishment of state commissions, planning districts and local planning committees. The governor of each state appoints a State Emergency Response Commission whose responsibilities include: designating emergency planning districts: appointing local emergency planning committees for each district; supervising and coordinating the activities of planning committees: reviewing emergency plans; receiving chemical release notifications; and establishing procedures for receiving and processing requests from the public for information about and/ or copies of emergency response plans, material safety data sheets, the list of extremely hazardous substances prepared as part of EPA's original Chemical Emergency Preparedness Program (which had been distributed to interested AIChE local sections) inventory forms and toxic chemical release forms.

*In short, the original AIChE local section initiative, to assist local communities in their voluntary emergency planning process, now has an increased significance since communities must adhere to these new directives.*

We urge local sections that have not already done so, contact designated officials responsible for such planning and offer the services of their members in technical aspects of the planning process.

If your section does not already have the AIChE Emergency Response Program Guidelines, please request same from the Washington Office or call Dr. Martin Siegel, Staff Director Government Relations at (202) 223-0650.

Those sections that are participating, may also request the new *"Hazardous Materials Emergency Planning Guide"* just released by the National Response Team. The NRT is composed of 14 Federal Agencies having major responsibilities in environmental, transportation and public health areas and is now the central body for planning, preparedness and response actions related to oil discharges and hazardous substance releases.

The "Guide" is available from the Washington Office of AIChE and replaces the earlier EPA interim guideline document.

*This material was prepared by AIChE's Washington Representative, Siegel • Houston & Associates, Inc.*
*Suite 804, 1901 L Street, N.W., Washington, D.C. 20036. Tel. (202) 223-0650*

# APCA'87

**June 21-26, 1987**
**Exhibition: June 23, 24, 25**
**The Jacob K. Javits**
**Convention Center**
**New York City**

### Technical Sessions

You have the opportunity to attend any of 90 technical sessions during a five day technical program. You may choose sessions from among nine broad areas:

- toxic air pollutants
- hazardous waste management
- control equipment and technology
- risk assessment and risk management
- indoor air quality
- legal and regulatory issues
- acidic deposition
- environmental measuring and modeling
- special environmental issues

### Exhibition

You also have the opportunity to meet the world's leading suppliers of:

- emission and ambient monitoring equipment for criteria and toxic pollutants
- consulting services for designing, auditing and permitting
- control equipment for criteria pollutants, VOCs and toxic pollutants
- hazardous waste treatment, storage and disposal methods including incineration
- indoor air and personal monitoring systems
- computerized control, management and data handling systems
- education, publishing and other professional associations
- U.S. EPA, and other governmental agencies and departments

### Committee Deliberations

Informally, you can engage in technical deliberations with your peers during the meetings of APCA's coordinating committees. You can select from any of more than 50 topics in six broad areas:

- Sources
- Effects
- Control Technology
- Control Program Administration
- Basic Science and Technology
- Waste

### Education Courses

You can enhance your environmental technical/managerial skills or advance your understanding of the subsequent technical sessions by attending any of 16 education courses. Both continuing education and refresher courses are offered on leading edge environmental topics.

### Supplementary Programs

APCA'87 offers technical tours, job placement assistance service for both employees and employers, student programs, spouses' programs, airfare discounts, social events and the concurrent meetings of other professional organizations.

**To receive complete details and registration forms, complete and return this coupon; or, write or phone: Sharon DeAndrea, APCA, P.O. Box 2861, Pittsburgh, PA 15230, USA—Tel: 412-232-3444.**

## You can determine how the many pieces of APCA'87 fit together to meet your needs and responsibilities.

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☐ Send me an Exhibition Prospectus.

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## Reducing Risks From Environmental Chemicals Through Biotechnology

### Conference in Seattle, WA, July 19-22, 1987

**Goal:** To stimulate scientifically sound applications of existing and engineered micro-organisms to the control of pesticides, solvents, and other chemical pollutants in the environment. Microbial ecology, environmental microbiology, genetic engineering, and site-specific applications will be presented and evaluated in intensive discussions.

**Methods: Applying Molecular Biology to Environmental Protection**
Microbial Ecology
Manipulating Organisms
Bioreactors and other engineering developments

**Applications: Chemical and Environmental Targets**

Chemicals: pesticides, organic solvents, halogenated compounds
Sites for Clean-Up (combining microbial and engineering methods): chemical spills, waste sites, contaminated groundwater, oil sumps, coal cleaning.

**Policy Issues: Assessment, Communication and Management of Environmental Risks**

Regulatory Approaches, Corporate Strategies, Public Participation

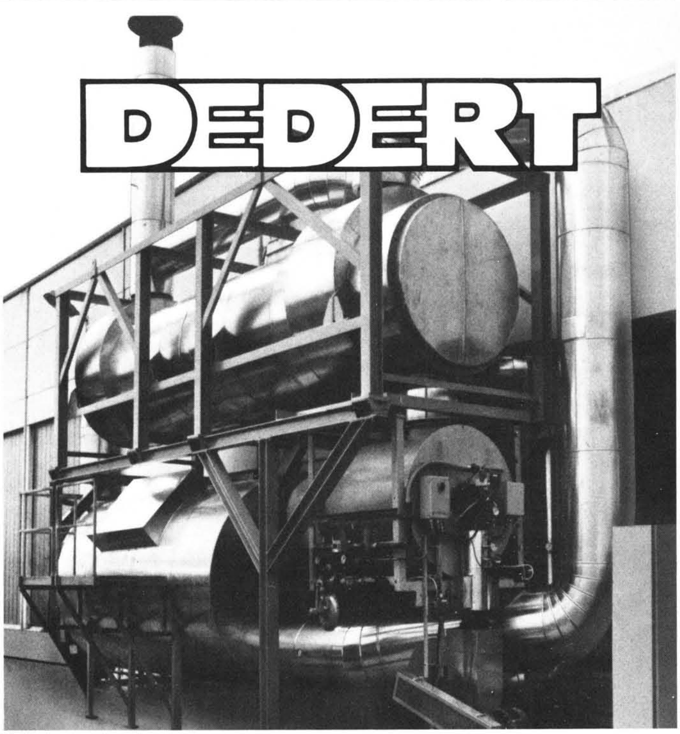
**Sponsored by**

American Institute of Chemical Engineers
Water Pollution Control Federation
Environmental Protection Agency
ECOVA Corporation
U.S. Air Force Engineering Center
University of Washington
Council for Research Planning
Other Agencies & Corporations Pending

**Registration Information**

Dr. Gilbert Omenn, Marge Falkner, University of Washington, SC-30, Seattle, WA 98195, (206) 543-1144

Poster presentations are warmly invited, poster abstracts will be published, as will roundtable discussions, in the post-conference book (Plenum Press).



# Books

**Modeling Remedial Action at Uncontrolled Hazardous Waste Sites,** S. H. Boutwell et al., Noyes Publications, Park Ridge, New Jersey, 1986, $48.00, 440 p.p.

**Proceedings of the 1986 Hazardous Material Spills Conference** (St. Louis, MO), Government Institute, Rockwell, Maryland, 1986, $64.00, 565 p.p.

**Management of Hazardous Waste Treatment/Storage/Disposal Facilities,** Technomic Publishing, Lancaster, Pennsylvania, 1986, $64.00, 311 p.p.

**Contaminated Surface Soils: In-Place Treatment Techniques,** R. Sims et al., Noyes Publications, Park Ridge, New Jersey, 1986, $62.00, 536 p.p.

**Hazardous Chemicals Data Book,** 2nd edition, G. Weiss, Sr., Noyes Publications, Park Ridge, New Jersey, 1986, $98.00, 1,069 p.p.

**The Common Sense Approach to Hazardous Materials,** F. L. Fire, Fire Engineering, New York, New York, 1986, 369 p.p.

**Quantitative Risk Assessment of Environmental and Occupational Health,** William H. Hallenbeck and Kathleen M. Cunningham, Lewis Publishers, Inc., 121 South Main Street, Chelsea, Michigan, 1986, $35.95, 202 p.p.

**Environmental Ethics for Engineers,** Alastair S. Gunn and P. Aarne Vesilind, Lewis Publishers, Inc., 121 South Main Street, Chelsea, Michigan, 1986, hardcover $18.95, softcover $13.95, softcover class order $10.95, 153 p.p.

# Conferences

**March 30-April 3, 1987—Vulnerability of Soil and Groundwater to Pollutants—VSGP '87**

Organized by the National Institute of Public Health and Environmental Hygiene, this conference will focus on an essential element in the wide range of research topics involved, such as the vulnerability of soil and groundwater with respect to their multifunctional character. Subjects to be covered are: development of monitoring strategies, data collection, interpretation of data, modeling and mapping. Special attention will be given to the interaction between top soils and groundwater bodies and to the spatial and temporal variability of parameters. For further information contact: VSPG '87 c/o Klvl, P.O. Box 30424, 2500 GK The Hague, The Netherlands. The conference will be held at the Grand Hôtel 'Huis ter Duin', Noordwijk aan Zee, situated South of Amsterdam.

**June 24-25, 1987—Symposium on Distillate Fuel System Contamination**

The American Society for Testing and Materials (ASTM) Committee D-2 on Petroleum Products and Lubricants will be sponsoring this meeting that will be held in June at the Weston Hotel in Cincinnati, Ohio. The three sessions of the symposium will focus on Type and Effects of Fuel Contamination, Prediction and Detection of Contamination Problems in Distillate Fuels, and Prevention Techniques and Procedures For Use in Contaminated Distillate Fuels. A Special Technical Publication (STP) based on the symposium proceedings is anticipated by ASTM. Advance registratin is strongly recommended. To receive a complete program booklet, including preregistration and hotel information, contact Staff Manager Earl Sullivan, ASTM Standards Development Division, 1916 Race Street, Philadelphia, PA 19103, or call (215)299-5514. Additional information is available from Symposium Chairman Howard Chesneau, Fuel Quality Service, Inc., Box 493, Flowery Branch, GA 30542, or call (404)945-7139.

**October 28-29, 1987—Safety in the Environment: Trends for the Future**

The Scottish Branch of the Institution of Chemical Engineers will be sponsoring this conference which will be held in Glasgow, Scotland. The integration of many aspects of safety in the environment and its impact on people will be the theme during the two day conference. Over twenty papers will be presented and four sessions will examine the following issues: Environmental Engineering, the connection between maintenance of the environment and maintenance of safety; Motivation and Occupational Health, improvement of performance in the work place by increasing awareness of weaknesses in operational practice; Pipelines, monitoring and experience of pipeline operation; and Onshore/Offshore Interchange, a symposium for the general exchange of ideas for the benefit of both sections of the processing industry. The conference is intended primarily for the "hands on" engineer and middle management. For further details write—The Conference Section, The Institution of Chemical Engineers, 165-171 Railway Terrace, Rugby. CV21 3HG LONDON, or call (0788) 78214.

# Treatment of a Landfill Leachate in Powdered Activated Carbon Enhanced Sequencing Batch Bioreactors

**Wei-chi Ying, Robert R. Bonk, Stanley A. Sojka**

Occidental Chemical Corporation, Grand Island Technology Center, Grand Island, NY 14072

*Addition of powdered activated carbon (PAC) significantly improved treatment of a chemical waste landfill leachate in sequencing batch bioreactors (SBRs). Concentrations for many of the monitored halogenated organic compounds in the effluent were below their respective detection limits. Excellent treatment efficiency was achieved under a variety of operating conditions: wastewater composition, feed rate, hydraulic retention time, organic loading, PAC dosages, biomass and PAC concentrations in the bioreactors. The PAC-SBR performance was unaffected when wastewater feeding was suspended during weekends and holidays. The PAC-SBR treatment cost is much lower than either that of the conventional granular activated carbon adsorption technology or the two-stage process of biodegradation and carbon treatment.*

## INTRODUCTION

The Hyde Park Landfill site is located in an industrial complex in the extreme northwest corner of the Town of Niagara, New York (Figure 1). The site is roughly triangular in shape and occupies approximately 6.1 hectares. The Hyde Park Landfill was used from 1953 to 1975 as a disposal site for an estimated 73000 metric tons of chemical waste, including halogenated organics. A compacted clay cover was placed over the landfill in 1978, and a tile leachate collection system was installed around the perimeter in 1979.

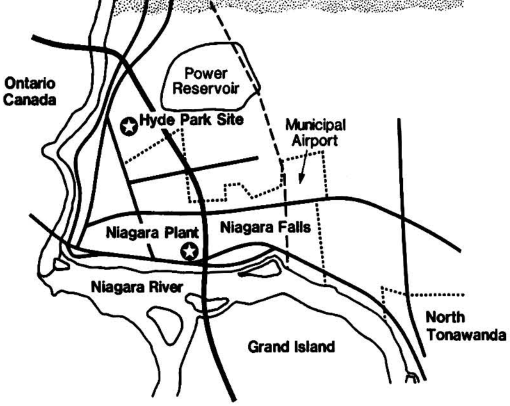


Figure 1. Location of the Hyde park Landfill site.

The leachate is collected in a sump, at the end of the tile system, and is then pumped to a two-compartment lagoon. The contents of the first lagoon compartment are allowed to separate, and the supernatant overflows by gravity into the second compartment. From here it is trucked to the treatment site located at the nearby Niagara Plant. The leachate production rate for the last three years averaged about 230 cu m per week. Additional leachate collection systems at Hyde Park and other sites will soon be constructed, and the total volume of wastewaters to be treated will increase substantially. At the treatment site, the trucked leachate is mixed with plant wastewaters and is stored in four storage tanks, each about 90 cu m in capacity. After pH adjustment, sometimes necessary to insure that pH of the plant discharge is between 5.0 and 10.0, and settling of suspended solids, the combined wastewater is pumped through an on-line 50μ bag filter, and the filtrate then is treated in a two-stage activated carbon adsorption system. In the first stage of treatment, the wastewater downflows through two smaller adsorbers (900 kg of Calgon F-300 each) in series for removal of carry-over organic liquids. Dissolved organic compounds are removed in the second stage adsorption system consisting of three larger serial adsorbers (9000 kg of Calgon Service carbon each). The effluent, which meets the treatment criteria (see Table 1), is discharged to a municipal sewer.

The present wastewater treatment by the conventional adsorption technology, although producing a suitable quality effluent, is not the best long-term solution. The adsorption system would have to be substantially expanded

TABLE 1. DISCHARGE LIMITS OF FINAL EFFLUENT

| Parameter | Maximum concentration[a] |
|---|---|
| pH | 5-10 |
| Phenol | 1 mg/L |
| TOC (excluding Methanol), or | 300 mg/L |
| TOC (total) | 1000 mg/L |
| Trichloroethylene | 10 ug/L |
| Tetrachloroethylene | 10 ug/L |
| Monochlorobenzene | 10 ug/L |
| Monochlorotoluene | 10 ug/L |
| Benzene | 10 ug/L |
| Trichlorobenzenes | 10 ug/L |
| Tetrachlorobenzenes | 10 ug/L |
| Monochlorobenzotrifluoride | 10 ug/L |
| Hexachlorocyclobutadiene (C-46) | 10 ug/L |
| Hexachlorocyclopentadiene (C-56) | 10 ug/L |
| Hexachlorocyclohexanes (C-66) | 10 ug/L |
| 2, 4, 5-trichlorophenol | 10 ug/L |
| Endosulfan | 10 ug/L |
| Mirex | 1 ug/L |
| 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin | not detectable |

a. Except for pH

to handle the expected increase in wastewater volume. The future carbon consumption rate would rise accordingly; the cost forecast for carbon adsorption service alone is about 21 million dollars over the next ten years. Clearly there is a strong economic incentive to explore other treatment technologies. The technical impetus derives from the fact that most persistent organic compounds are readily adsorbed on activated carbon and many of them would eventually be biodegraded given the long holding time in the adsorbed state [*1*, *2*]. Addition of powdered activated carbon (PAC) to the aeration tank of an activated sludge system would produce many benefits: higher degree of organic removal, better settling sludge with excellent dewaterability, improved nitrification, more resistance to shock loadings of wastewater constituents and/or flowrate [*3*, *4*]. In many instances, PAC enhanced biological treatment may produce a high quality effluent comparable to that from two-stage treatment of biodegradation followed by activated carbon adsorption [5]. Because of the successful bench- and pilot-scale treatment of Hyde Park leachate in sequencing batch bioreactors (SBRs) and the high adsorptive capacities of activated carbon for the leachate constituents [6], the bio-physicochemical PAC enhanced SBR (PAC-SBR) wastewater treatment technology was selected as a candidate process to best meet the future requirements for leachate disposal.

## EXPERIMENTAL SECTION

### Analytical methods

Extensive efforts were made in this investigation for identification and quantification of constituents of raw, pretreated, SBR-treated, and PAC-SBR treated wastewater samples. Measurements for parameters commonly used for characterization of wastewater were made in accordance with the methods given in *Standard Methods* [7]. These parameters include: pH (Section 423), total organic carbon (TOC, 505), biological oxygen demand (BOD, 507), chemical oxygen demand (COD, 508A), total dissolved solids (TDS, 209C), suspended solids (SS, 209D), volatile suspended solids (VSS, 209E), orthophosphate phosphorus ($PO_4$-P, 424F), acid-hydrolyzable phosphorus (acid-P, 424B), total phosphorus (total-P, 424C), ammonia nitrogen ($NH_4$-N, 417B), nitrate nitrogen ($NO_3$-N, 418 B), nitrite nitrogen ($NO_2$-N 419), total kjeldahl nitrogen (TKN, 420 B), dissolved oxygen (DO, 421F), oxygen consumption rate (213A), turbidity (214A), and settled sludge volume (213B). Total organic halide (TOX) was anlayzed by a Dohrmann DX-20 TOX analyzer using EPA Method 450.1. Concentrations for chlorendic acid (HET acid), phenol, benzoic acid, and o-, m-, p-chlorobenzoic acids (CBAs) were estimated by a high performance liquid chromatography method, with a Perkin-Elmer Model 3B, adapted for analysis of the wastewater samples [6]. Analyses of samples for the compounds listed in Table 1 were performed by Central Science personnel of Occidental Chemical according to the protocols approved by the New York State Department of Environmental Conservation. The standard scintillation counting techniques were employed for measuring $^{14}$C-labelled 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (2, 3, 7, 8-TCDD, from Cambridge Isotope Laboratories, Inc., Woburn, Mass. 01801) and polychlorinated biphenyls Aroclor 1254 (PCBs A-1254, from Amershan Corp., Arlington Heights, Ill. 60005.

Concentration of pollutants in raw leachate and the combined wastewater fluctuated widely over the study period; TOC had a range from 850 to 10000 mg/L and SS from 200 to 2000 mg/L. Characteristics of typical raw and pretreated (neutralization, aeration, and sedimentation) leachates are shown in Table 2.

### Adsorption Isotherms

Adsorption isotherm experiments were performed for testing the adsorptive capacity of PAC, biomass, and pretreatment precipitates for HET acid, $^{14}$-C-labelled 2, 3, 7, 8-TCDD and PCBs A-1254. The Freundlich adsorption isotherm model was utilized to correlate the adsorptive capacity (X/M, mg adsorbed/g carbon) with the residual concentration ($C_f$, ug or mg/L) for estimating the magnitude of organic removal due to adsorption. The Freundlich model has the following form:

$$X/M = k \times C_f^{1/n}$$

where k, and 1/n are constants characterizing the adsorption isotherm [8].

### Biodegration Study

Soon after the present adsorption treatment began, large populations of bacteria were found in the adsorber effluent. Similar observations of bacterial growth in carbon adsorbers were reported [9]. The TOC, COD, and concentrations for some major organic constituents of a refrigerated raw leachate sample were found to decrease over time. The rate of concentration reduction increased when the sample was stored at room temperature. The BOD to TOC ratios for several leachate and the combined wastewater samples were all greater than 2, indicating

TABLE 2. CHARACTERISTICS OF TYPICAL RAW AND PRETREATED HYDE PARK LEACHATES

| Parameter[a] | Raw leachate | Pretreated leachate[b] |
|---|---|---|
| pH | 4.3 | 7.5 |
| TOC | 3500 | 3200 |
| COD | 10040 | 9200 |
| BOD | 7500 | 7200 |
| SS | 900 | 80 |
| VSS | 300 | 40 |
| TDS | 25700 | 22400 |
| $PO_4$-P | <1 | <1 |
| Acid-P | 3 | 3 |
| Total-P | 131 | 92 |
| $NH_4$-N | 150 | 130 |
| TKN | 180 | 160 |
| $NO_3$-N | 20 | 20 |
| $NO_2$-N | <5 | <5 |

a. All values, except pH, are given in mg/L.
b. Pretreatment consisted of neutralization with NaOH to a pH of 7.5, two hours of aeration, and two hours or longer of settling.

that most organic compounds in these samples were readily biodegradable. Results from studies on bio-utilization of specific organic compounds by bacteria isolated from the Hyde Park Landfill site demonstrated that several strains of bacteria present in the landfill site were capable of metabolizing many of the more persistent leachate constituents [6]. Biological processes were therefore evaluated for treating the combined wastewater before entering the existing activated carbon adsorption system.

SBR biotreatment consists of five sequential steps: FILL REACT, SETTLE, DRAW, and IDLE. The wastewater is fed, during FILL, to a tank which contains acclimated activated sludge from the previous cycle. Aeration and mechanical mixing are provided while feeding, or during REACT, to enhance the rate of aerobic biodegradation. After the mixed liquor is biologically stabilized, air and mixing are stopped, and clarification takes place in the SETTLE step. During DRAW, the clear supernatant is withdrawn from the reactor for direct discharge or, if needed, additional treatment. The IDLE period finally completes the SBR cycle. The five SBR steps are often overlapped, and one or two steps may be omitted in a particular treatment cycle. The withdrawal of effluent may start as soon as a clear zone of supernatant is formed, and the wastewater feeding may begin immediately after the completion of the DRAW step of the last SBR cycle [*10*]. Many combinations of feeding, aeration, and mixing strategies are possible. The required nutrients are either supplemented to the feed or added directly to the bioreactor. The sludge wasting is accomplished by removing a portion of the settled sludge in the DRAW or IDLE step. The optimum SBR operating and cycle schedules must be experimentally established for a wastewater to achieve the specific treatment objectives. The SBR biotreatment is essentially a fill-and-draw activated sludge process. Its operation and control for bench-scale experiments are simple, and the requirements for laboratory space and wastewater volumes are small. Relative to the continuous activated sludge process, better comparative study is possible since more parallel SBR units can be operated simultaneously using smaller tanks. It is therefore often the process of choice for study of wastewater treatability [*11, 12*]. The advantages of more complete treatment [*13*], greater operational flexibility to accommodate changing feed characteristics, intermittent treatment [*14*], and single tank for biodegradation and sludge separation make the SBR process an attractive technology for treating municipal and industrial wastewaters [*15, 16*]. The successful bench- and pilot-scale investigations already demonstrated that significant carbon saving was possible with SBR biotreatment of leachate before carbon adsorption [*6*].

### PAC-SBR treatment

A feasibility study on PAC-SBR treatment of leachate was conducted to determine whether the improved treatment by simultaneous adsorption and biodegradation in a SBR would produce an acceptable effluent without the post-treatment in a granular activated carbon adsorber. This was indeed accomplished with the simple addition of PAC to a SBR, near the end of REACT, operated at a hydraulic retention time (HRT) of 5 days or less. The PAC dosage, 0.45 g of Westvaco Nuchar SA (PAC A) per daily leachate feed volume of 150 ml, was just below the expected carbon requirement of the two-stage SBR-adsorption process (0.54 g based on a carbon exhaustion rate of 3.6 g/L for treating a 5000 mg TOC/L leachate and a 90% reduction in the carbon cost due to SBR biotreatment). Table 3 presents the feasibility study results showing significant improvement in effluent quality with the addition of PAC. The PAC-SBR effluent continued to be much better than that of the control unit three weeks after the PAC addition was stopped. It was important to note that the removal of the persistent HET acid in the PAC-SBR was consistently more than that predicted by the adsorption isotherm for the SBR-treated leachate [6]. A comprehensive PAC-SBR treatability study program was therefore undertaken to define the PAC requirement and to optimize the bio-physicochemical treatment operations. The operating and cycle schedules for the eight 1-L reactors employed in the treatability study program are presented in Table 4; the routine maintenance, sampling, and monitoring schedule is summarized in Table 5. The schematic drawing of a PAC-SBR used in the feasibility and treatability studies is given in Figure 2.

## RESULTS AND DISCUSSION

### Start-up procedure

About 5 L of return activated sludge (MLSS = 6000 mg/L) from a nearby POTW (Wheatfield, NY) was used to seed a 10-L SBR bioreactor. The SBR was then fed, over a four-day period at an increasing daily feed volume of Hyde Park leachate to 2 L/d. The amount of effluent dis-

TABLE 3. FEASIBILITY STUDY RESULTS OF PAC-SBR TREATMENT OF HYDE PARK LEACHATE[a,b]

| Sample | Date | 10/9 | 10/25 | 11/7 | 11/15[c] | 11/24 | 12/1 | 12/14 |
|---|---|---|---|---|---|---|---|---|
| Feed | volume | 75 | 150 | 150 | 150/225 | 150 | 300 | 275 |
| | TOC | 10575 | 5580 | 5570 | 5570 | 3080 | 840 | 3210 |
| | TOX | 1062 | 660 | 640 | 520 | 650 | 141 | 390 |
| | HET acid | 455 | 335[d] | 280[d] | 250[d] | 320 | 57 | 145 |
| | phenol | 1553[d] | | | | 1135 | 201 | 780 |
| Control SBR effluent | TOC | 417 | 391 | 494 | 436 | 296 | 132 | 184 |
| | TOX | 316 | 267 | 325 | 265 | 243 | 68 | 155 |
| | HET acid | 270 | 149 | 170 | 231 | 166 | 52 | 125 |
| | phenol | 17.5 | 20 | | 10 | 10 | 2.5 | 12 |
| PAC-SBR[c] effluent | TOC | 439 | 157 | 164 | 207 | 125 | 120 | 144 |
| | TOX | 319 | 42 | 46 | 88 | 41 | 52 | 134 |
| | HET acid | 279 | 46 | 28 | 36 | 16 | 38 | 104 |
| | phenol | 7.5 | 0.5 | | 0.5 | 0.5 | 0.5 | 1.25 |

---

a. All units were on a 24-hour SBR cycle-batch feed, 20 hours of aeration, and 4 hours of settling and idle. Liquid volume after FILL (working volume) was 750 ml. The MLSS of the control SBR was maintained at 10000 mg/L. The biotreatment was performed at the room temperature of 20°C.

b. Results are given in ml/day for feed volume and mg/L for all concentrations.

c. The PAC-SBR unit received 1.5X the leachate volume fed to the control SBR from 11/12 thru 11/18. This unit was a duplicate control SBR until 10/20 when 4.5 g of PAC A, which was presaturated with compounds remaining in the leachate after biotreatment by contacting with a large volume of effluent, was added; 0.45 g/d of fresh PAC A was added thereafter until 11/23 when the PAC addition was stopped. The MLSS of the PAC-SBR was 14000 mg/L after the first PAC addition; the PAC concentration was maintained at 6000 mg/L by wasting 75 ml of the mixed liquor per day after PAC supplementation.

d. Those samples were not acidified prior to analysis, and thus the values shown might be lower than the concentrations at the time of sampling.

TABLE 4. EXAMPLES OF PAC-SBR OPERATING AND CYCLE SCHEDULES

| | PAC-SBR Units<br>600 ml working volume, 24-hour cycle, 20°C<br>4-day hydraulic retention time (25% daily feeding) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Operating Schedule | 1C | 3A | 3B | 4A | 4B | 6A | 6B | 6C |
| Wastewater feed | ( | | | pretreated leachate | | | | ) |
| Sterilization of feed | ( | | | no | | | | ) |
| Bacterial supplementation | ( | | | no | | | | ) |
| Mixed liquor biological suspended solids, mg/L | 10000 | ( | | $10000^a$ | | | | ) |
| Mixed liquor PAC, mg/L | 0 | 3000 | 3000 | 4500 | 4500 | 6000 | 6000 | 6000 |
| PAC inventory, g | 0 | 1.8 | 1.8 | 2.7 | 2.7 | 3.6 | 3.6 | 3.6 |
| PAC dose, g/day | 0 | 0.09 | 0.18 | 0.135 | 0.27 | 0.18 | 0.18 | 0.36 |
| Mixed liquor wasting, ml/day | $VW^b$ | 30 | 60 | 30 | 60 | 30 | 30 | 60 |
| Time per SBR cycle, hour | | | | | | | | |
| FILL (air & mixing) | ( | | | $6^c$ | | | | ) |
| REACT (air & mixing) | ( | | | 14 | | | | ) |
| SETTLE | ( | | | 3 | | | | ) |
| DRAW | ( | | | $0.25^d$ | | | | ) |
| IDLE | ( | | | 0.75 | | | | ) |

---

a. Initial value at the beginning of PAC-SBR study; it gradually declined with the daily wasting of mixed liquor. The steady state mixed liquor biological solids concentration was dependent on the feed concentration and daily wasting volume.

b. The mixed liquor wasting volume of the control unit was calculated (see Note b in Table 5) to maintain a MLSS concentration of 10000 mg/L.

c. The PAC-SBR units were fed twice, 12.5% of working volume each time at the beginning and the end of FILL.

d. Effluent discharge was accomplished using a 100-ml pipet.

TABLE 5. ROUTINE MAINTENANCE, SAMPLING, AND MONITORING SCHEDULE FOR PAC-SBRs

| | Monday | Tuesday | Wednesday | Thursday | Friday |
|---|---|---|---|---|---|
| $pH^a$ | x | x | x | x | x |
| Turbidity | x | | x | | x |
| TOC | x | x | x | x | x |
| Settled sludge volume | x | | | x | |
| Mixed liquor SS/VSS | x/x | | | x | |
| Slude $wasting^b$ | | x | | | x |
| Effluent SS/VSS | | x/x | | | x |
| $NH_4$-N | | x | | | x |
| $NO_2$-N/$NO_3$-N | | x | | | x |
| $PO_4$-P | | x | | | x |
| TOX, HET acid, phenol, benzoic and chlorobenzoic $acids^c$ | | | | | |
| Chlorinated compounds listed in Table $1^d$ | | | | | |

---

a. Acid or base was used to maintain pH within 7.0-7.5 after REACT

b. The volume of the settled sludge to be wasted each time, VW (L):

$VW = VT \times (MLSS1 - MLSS2)/(MLSS1 \times TMV/SV)$

where, VT - working volume (L), after FILL,

TMV - the sample volume used in measuring the settled sluge volume ,

SV - settled sludge volume after two hours of settling,

MLSS1 - mixed liquor suspended solids (mg/L) before wasting,

MLSS2 - the MLSS to be maintained in the reactor.

Tapwater was used for making up the settled sludge volume wasted.

c. One measurement for each batch of new leachate feed, and once every two weeks for all effleunts.

d. One weekly composite sample each from No. 3A, 3B, and 4A.

charged was about 50% of the daily feed until the full SBR working volume (8 L) was attained. Within three weeks, the effluent TOC was stabilized at about 250 mg/L for a leachate feed having a TOC of 3000 mg/L. The biotreatment was accomplished at the room temperature of 20°C in the SBR which was operated under a 24-hr cycle (Table 4). No mass die-off of the seed sludge was observed, and the effluent SS was consistently less than 100 mg/L. Successful start-up was accomplished without the use of any supplementary sources of organic carbon [6]. When the MLSS increased to about 10000 mg/L, the liquid content of the 10-L SBR was divided evenly to eight 1-L units. A quantity of PAC A which had been presaturated with compounds remaining in the leachate after the biotreatment (by contacting with a large volume of effluent from the 10-L SBR) was then introduced to each PAC-SBR to provide a specified mixed liquor PAC concentration (Table 4). A small dose of PAC was added daily during the treatability study program. The leachate feed was prepared by the pretreatment procedure of neutralization, aeration, and sedimentation; ammonium hydroxide and phosphoric acid were supplemented to the leachate feed

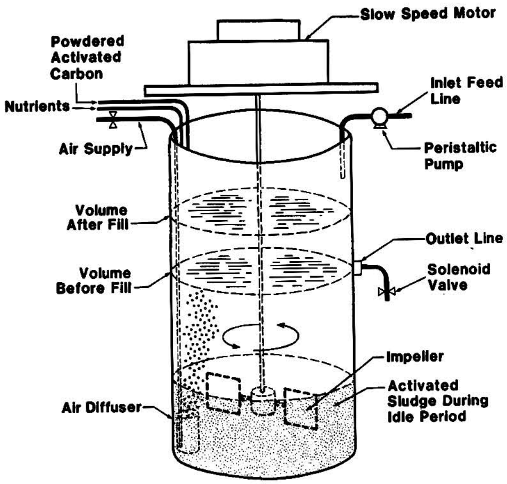


Figure 2. Schematic drawing of a PAC-SBR.

to a TOC/$NH_4$-N/$PO_4$-P ratio of 150/10/2 which was determined in the earlier study on SBR treatment of leachate [*6, 17*].

**Treatability study results**

Table 6 presents the treatment results in terms of reductions in TOC, TOX, HET acid, phenol, benzoic acid, and CBAs; Table 7 presents the reductions in TCDDs, PCBs, and five other halogenated compounds subjecting to the discharge limits (Table 1). The improvements in effluent quality due to the addition of PAC to the control SBR were apparent. Most importantly, the effluent from PAC-SBR 3A, the least PAC-dosed unit, had consistently met the discharge limits during the entire study period. The PAC supplementation rate was less than 4% of the estimated granular activated carbon requirement for treating the raw Hyde Park leachate - 0.09 vs. 3.7 g per 150 ml daily leachate feed (TOC = 3570 mg/L) [*6*]. The fact that TCDDs and PCBs were totally removed by the PAC-SBR treatment can be explained by the adsorption isotherms for $^{14}$C-labelled 2, 3, 7, 8-TCDD (Figure 3) and PCBs A-1254 (Figure 4). Both the solid precipitates (SS up to 2000 mg/L) produced in the pretreatment steps and biomass in the SBR (MLSS = 10000 mg/L) had contributed to the removal of TCDDs and PCBs. The significantly enhanced removal of these and other persistent halogenated organic compounds in the PAC-SBRs was due to the much higher adsorptive capacities of activated carbon relative to pretreatment precipitates and SBR biomass. The quality of effluents from the PAC-SBRs were much more stable, compared to the control unit (No. 1C), when the organic loading to the aeration tank was increased because of higher leachate TOC and/or more daily feed volume. This shock loading resistance was attributable to the large inventory of PAC (3000 to 6000 mg/L) in the mixed liquor. Nitrification and denitrification were observed in all bioreactors with no aeration during the last two hours of REACT. The PAC-SBR treatment can thus accomplish nitrogen removal as well [*18*].

**Intermittent operations**

The PAC-SBR treatment performance was nearly unchanged when the feeding was suspended on holidays, Saturday and/or Sunday. The REACT period for these units were extended over the weekend, with either continuous or periodic aeration and mixing during the extra time period. This resulted in slightly lower effluent TOC, more complete nitrification and/or denitrification. Normal cyclic operation was resumed from Monday through Fri-

TABLE 6. RESULTS OF PAC-SBR TREATMENT OF LEACHATE[a]

| PAC-SBR sample | TOC | TOX | HET acid | Phenol | Benzoic acid | m-CBA | p-CBA |
|---|---|---|---|---|---|---|---|
| | ( | | | mg/L | | | ) |
| Feed | 3570 | 440 | 150 | 820 | 1160 | 130 | 160 |
| 1C effluent | 286 | 196 | 102 | 3 | 6 | 20 | 16 |
| 3A effluent | 207 | 141 | 80 | <1 | 4 | 5 | 9 |
| 3B effluent | 179 | 114 | 77 | <1 | 2 | 4 | 7 |
| 4A effluent | 207 | 130 | 80 | <1 | 2 | 10 | 8 |
| 4B effluent | 143 | 83 | 51 | <1 | 2 | 5 | 5 |
| 6A & B effluent[b] | 179 | 106 | 71 | <1 | 2 | 3 | 7 |
| 6C effluent | 121 | 55 | 63 | <1 | 2 | 2 | 3 |

a. Samples were taken at the end of the treatability study program.
b. Average of the duplicate units.

TABLE 7. REMOVAL OF TCDDS, PCBS AND HALOGENATED ORGANIC COMPOUNDS IN PAC-SBRS

| PAC-SBR Sample | TCDDs[a] | PCBs[b] | Trichloro-benzenes | C-56 | 2, 4, 5 Tri-chlorophenol | Endosulfan | Mirex |
|---|---|---|---|---|---|---|---|
| | (ppt) | ( | | | ppb | | ) |
| 1C effluent | 1.5 | 9 | 68 | 37 | 39 | 51 | 26 |
| 3A effluent | $ND_{0.8}^{c}$ | $ND_2$ | $ND_{10}$ | $ND_{10}$ | $ND_{10}$ | $ND_{10}$ | $ND_1$ |
| 3B effluent | $ND_{0.8}$ | $ND_2$ | $ND_{10}$ | $ND_{10}$ | $ND_{10}$ | $ND_{10}$ | $ND_1$ |
| 4A effluent | $ND_{0.8}$ | $ND_2$ | $ND_{10}$ | $ND_{10}$ | $ND_{10}$ | $ND_{10}$ | $ND_1$ |
| 6C effluent | $ND_{0.8}$ | $ND_2$ | $ND_{10}$ | $ND_{10}$ | $ND_{10}$ | $ND_{10}$ | $ND_1$ |

a. 2, 3, 7, 8-TCDD and coeluting isomers.
b. Aroclor-1248.
c. $ND_x$ = Not detected at a detection limit of x ppt or ppb.

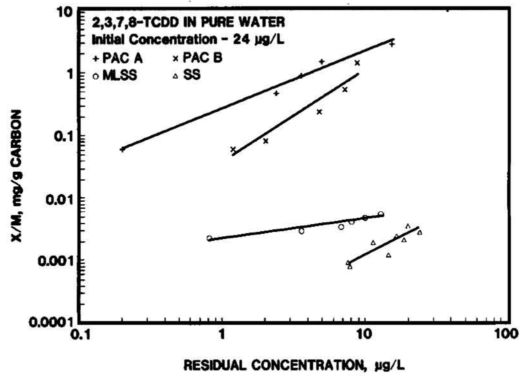


Figure 3. Freundlich adsorption isotherms for $^{14}$C-labelled 2, 3, 7, 8,-TCDD.

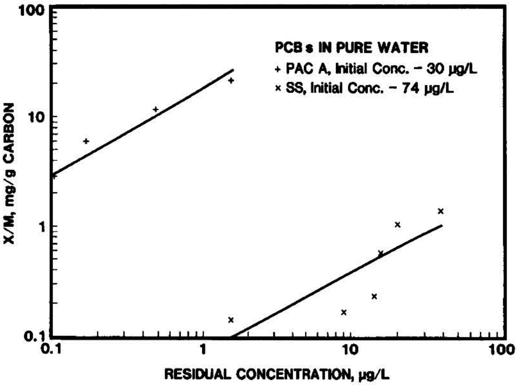


Figure 4. Freundlich adsorption isotherms for $^{14}$C-labelled PCBs A-1254.

day, and the same performance as the 7 days-a-week units was then observed. The ability to operate the PAC-SBRs in this manner would allow for a very flexible treatment schedule.

### Volatile compounds

Many aromatic and straight-chain halogenated hydrocarbons were present in Hyde Park leachate. Their concentrations were typically less than 5 mg/L, except for chlorotoluenes which occasionally approached 40 mg/L. Air stripping was found to be the predominant mechanism for their removals in the aerobic biological treatment system [*19*]. About 99% of the volatile constituents, which altogether accounted for about 5% of wastewater TOC, were air-stripped from the feed tank during pretreatment, and the rest were removed from the PAC-SBRs during aerated FILL and/or REACT. These compounds were easily separated from the air by carbon adsorption. With a vapor phase carbon adsorber installed for treating the exhaust gases, no air pollution would result from the PAC-SBR treatment system.

### Sludge disposal

Depending on the wastewater characteristics, 200 to 2000 mg of pretreatment precipitates per liter of feed were produced by neutralization, aeration, and sedimentation. It was mainly ferric hydroxide which included adsorbed organic compounds. As much as 62% of HET acid in the raw wastewater was removed by iron precipitation; other constituents were removed to lesser extents. The sludge

TABLE 8. EXPECTED SAVING IN LEACHATE TREATMENT COST WITH PAC-SBR PROCESS

| Time Period (months) | Flowrate (m³/d) | TOC[a] Loading ( | Carbon[b] Usage kg/d | Carbon[c] Saving ) | Cost Saving[d] |  |
|---|---|---|---|---|---|---|
|  |  |  |  |  | $/d | $1000/yr |
| 1 thru 6 | 95 | 142 | 991 | 961 | 1590 | 580 |
| 7 thru 12 | 295 | 215 | 1442 | 1399 | 2313 | 844 |
| 13 thru 18 | 250 | 202 | 1361 | 1320 | 2183 | 796 |
| 19 thru 24 | 144 | 170 | 1170 | 1135 | 1877 | 685 |
| 25 thru 30 | 144 | 170 | 1170 | 1135 | 1877 | 685 |
| 31 thru 36 | 144 | 170 | 1170 | 1135 | 1877 | 685 |
| 37 thru 120 | 144 | 170 | 1170 | 1135 | 1877 | 685 |
|  |  |  | 10-year Average Saving |  |  | $693,700/year |

---

a. The first 68 m³/d at 1700 mg TOC/L; the next 45 m³/d at 1 000 mg TOC/L; the rest at 300 mg TOC/L.
b. 12 g/L for the first 68 m³/d; 6.6 g/L for the next 45 m³/d; 1.8 g/L for the rest.
c. 97% reduction in carbon exhaustion rate using PAC-SBR process.
d. $1.65/kg carbon. All costs are in 1984 U.S. dollars.

SBR Treatment System - design TOC loading = 181 kg/d
average TOC loading = 173 kg/d

|  |  | $/year |
|---|---|---|
| 1. Carbon saving |  | 693,700 |
| 2. Operating labor, misc. costs[a] |  | ( 0 ) |
| 3. Maintenance[a] |  | ( 50,000 ) |
| 4. Electrical power[b] |  | ( 20,000 ) |
| 5. Sludge disposal[c] |  | ( 25,000 ) |
| 6. Analytical[a] |  | ( 23,000 ) |
| 7. Nutrients and chemicals[d] |  | ( 4,600 ) |
|  | Net Saving | $ 571,000/year |

---

a. Cost over the expanded adsorption operation required in the near future.
b. $0.06/kWh.
c. Total sludge production rate - 1.02 g/g TOC; dewatered sludge - 30% solid, disposal costs - $0.10/kg.
d. Supplementing $NH_3$ and $H_3PO_4$ to a TOC/$NH_4$-N/$PO_4$- P ratio of 150/10/2.

was well compacted in the feed tank, to about 7% solids, and easily dewatered by either vacuum or press filtration, to more than 30% solids. Biomass yield was estimated at 0.20 mg/mg feed TOC for the control SBR and would slightly be lower in the PAC-SBRs [5, 6]. The initial MLSS settling rate was estimated at 3 cm/min. The wasted MLSS from the PAC-SBRs was already aerobically stabilized, and no significant volume reduction was observed after 10 days of aerobic digestion. The settled sludge contained about 3.5% solids, and the dewatered sludge had about 30% solids.

### Carbon saving

Table 8 presents the expected saving, using the PAC-SBR process compared to the existing granular activated carbon adsorption process, in the future Hyde Park leachate treatment costs. The PAC-SBR treatment of leachate is more cost effective than the two-stage SBR-granular activated carbon treatment because of the overall lower carbon consumption rate and because there is no need for several polishing carbon adsorbers with their associated piping, pumps, and controls.

## SUMMARY

. Approximately 73000 metric tons of chemical waste are contained in the Hyde Park Landfill site, in Niagara Falls, New York. About 40000 liters a day of leachate is collected, trucked to a nearby chemical manufacturing plant, and then treated with plant wastewaters by activated carbon adsorption. Because of additional leachate volume to be treated in the near future, the carbon consumption rate is expected to rise accordingly. The organic constituents of this leachate, which accounts for about 60% of the combined wastewater volume but more than 80% of the total organic loading to the existing adsorption system, were found to be easily biodegraded. Biological pretreatment of the combined wastewater in sequencing bath reactors (SBRs) was capable of reducing the carbon requirement by 90%. An even more attractive alternative is biophysicochemical treatment of leachate in powdered activated carbon enhanced sequencing batch bioreactors (PAC-SBRs).

Addition of powdered activated carbon (PAC) significantly improved waste treatment performance of SBRs. Because of the concurrent dual organic removal mechanisms, i.e., adsoprtion of persistent compounds on PAC and biodegradation by the mixed culture bacteria, in these PAC-SBR units, the effluents were able to meet very stringent limits on a broad spectrum of parameters. Concentrations for many of the monitored halogenated organic compounds in the effluent were below their respective detection limits.

Excellent treatment efficiency was consistently achieved in bench-scale PAC-SBR units under a variety of operating conditions: wastewater composition, feed rate, hydraulic retention time, organic loading, PAC dosages, biomass and PAC concentrations in the bioreactors. The large inventory of PAC in the mixed liquor (3000 to 6000 mg/L) served as an ideal buffer for preventing any adverse effects due to sudden changes in wastewater characteristics. Some persistent organic compounds might have been biodegraded due to bacterial acclimation which was made possible because of the long holding time of these compounds in the adsorbed state. Furthermore, the performances of those PAC-SBR units without wastewater feeding during weekends and holidays were unaffected. High degree of operational flexibility and low demand for manual attention were demonstrated in the treatability study. The PAC-SBR wastewater treatment process would realize most advantages claimed for the SBR and the powdered activated carbon activated sludge (PACT) processes.

The PAC dosage required for treating Hyde Park leachate (TOC up to 8000 mg/L) was determined to be less than 4 percent of the carbon exhaustion rate of the existing adsorption treatment process. The small PAC dosage requirement was a direct consequence of continuing biodegradation of the adsorbed organics. The wastewater treatment cost of this integrated process is substantially lower than either that of the granular activated carbon adsorption process or the two-stage process of biotreatment in SBR followed by carbon adsorption. The PAC-SBR process would be equally attractive in treating other high TOC industrial wastewaters.

## ACKNOWLEDGMENT

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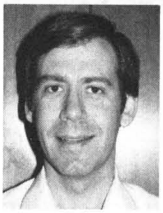
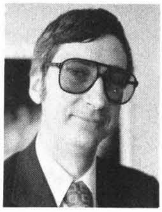


**Robert B. Bonk** is an associate chemist of Environmental Technology at the Grand Island Technology Center, New York, of Occidental Chemical Corporation. He has participated in a variety of environmental control research and development projects including biological, chemical, and physical processes for treating industrial wastewaters. He earned a B.S. in Chemistry from Rochester Institute of Technology and an M.B.A. from Canisius College. He is enrolled in the graduate Water Resources and Environmental Engineering program at State University of New York at Buffalo.

**Wei-chi Ying** is an associate scientist for Occidental Chemical Corporation and an adjunct associate professor of Environmental Engineering at State University of New York at Buffalo. He was a visiting professor at East China Institute of Chemical Technology in 1983. His work on modelling and application of biological carbon adsorption process won the 1979 Nalco Award for significant research in water and wastewater treatment. He earned a B.S. in Chemical Engineering from Tunghai University (Taiwan), an M.S. in Chemical Engineering from the University of Toledo, an M.S.E. and a Ph.D. in Environmental Engineering from the University of Michigan.



**Stanley A. Sojka** is the manager of Special Environmental Programs for Occidental Chemical Corporation. He is in charge of waste landfill site remediation activities including the selection of appropriate technologies for treating liquid and solid wastes. He continues to play a major role in the R&D projects on the use of genetically engineered bacteria for pollution control purposes. He has received numerous awards for outstanding research and for professional service. He has a B.S. in Chemistry from Canisius College and a Ph.D. in Organic Chemistry from Indiana University. He conducted post doctoral research at University of Basel (Switzerland) and served on the Chemistry faculty at Trinity College in Washington, D.C.

# Flue Gas Scrubbing Process For Sulfur Dioxide and Particulate Emissions Preceding $CO_2$ Absorption

**Jack D. Brady**

Andersen 2000 Inc., 306 Dividend Drive, Peachtree City, Georgia 30269

*This article describes a 2-stage scrubbing process which utilizes sodium hydroxide or sodium carbonate as the neutralizing chemical for sulfur dioxide and sulfur trioxide emissions to remove contaminants from gas streams preceding $CO_2$ absorption processes. Amine absorption processes are adversely affected by sulfur dioxide in the gas stream, and it is desirable to reduce sulfur dioxide concentrations to less than 5 ppm (vol). Conventional flue gas desulfurization processes do not achieve outlet concentrations at this level. With appropriate controls on pH, ionic strength, and liquid recirculation rates, the sodium alkalies can achieve these outlet concentrations. When concentrations of sulfur dioxide absorbed become sufficiently large to make the economics of a simple throw-away process uneconomical, the waste solutions can be regenerated in the double-alkali process by reacting them externally from the scrubbing system with calcium compounds. This process is also described. Particular emphasis is placed on process design for reliability. Materials of construction, process controls, and process chemistry are discussed.*

## ACID GAS REMOVAL

Many industrial steam boilers and fossil fuel-fired electric utility plants are located in areas where large volumetric flow rate $CO_2$ projects are being considered. The flue gases from these boilers provide a relatively low cost $CO_2$ source. Inherent in use of these $CO_2$ sources is the need for the solvent to tolerate relatively high oxygen concentrations without degradation and the need to remove virtually all of the contaminating acid gases and particulate matter from the source gas prior to $CO_2$ absorption. Oxygen tolerance for amine absorbers has been the subject of research efforts which have resulted in greatly improved, oxygen tolerant amine absorbers. Acid gases, such as $SO_2$, $SO_3$, HCl, NO, and $NO_2$, result in high amine consumption if they are not removed from the gas stream prior to the $CO_2$ absorption step. Fly ash from coal and oil-fired sources will also result in high amine consumption if allowed into the $CO_2$ absorption step.

Most acid gas absorption systems have been designed to comply with air pollution control regulations, particularly for $SO_2$ from coal and oil-fired sources. These regulations, while requiring as high as 95% $SO_2$ removal efficiency, have not resulted in systems which can economically produce sulfur dioxide concentrations as low as are desired for the amine absorbers. We are aware of no utility plant in the United States that is required to exhaust flue gas with less than 100 ppm (vol) sulfur dioxide. Ideally, the amine systems operate with incoming sulfur dioxide concentrations of less than 1 ppm (vol). The lime and limestone systems used for sulfur dioxide absorption are not capable of achieving concentrations less than 100 ppm without stoichiometric excesses of lime or limestone on the order of five times actual reaction requirements. Even then, the absorbers used would be prohibitively large and would still produce outlet concentrations of greater than 20 ppm (vol).

Sodium hydroxide or sodium carbonate-based scrubbing liquids are capable of achieving absorption efficiencies which can yield very low sulfur dioxide outlet concentrations. There are deficiencies in most of the common processes using sodium based scrubbing liquids, in that pH levels must be adjusted to greater than 8.0 to achieve 1 ppm $SO_2$ or less in a conventional absorber. When pH levels are adjusted this high, $CO_2$ absorption takes place and competes with the sulfur dioxide absorption, resulting in high alkali consumption. The $CO_2$ losses are significant.

## SYSTEM CHEMISTRY

When either sodium carbonate or sodium hydroxide react with sulfur dioxide, they produce solutions containing sodium sulfite ($Na_2SO_3$), sodium bisulfite ($NaHSO_3$), and sodium sulfate ($Na_2SO_4$), sometimes with free alkali and sometimes with free sulfurous acid ($H_2SO_3$). Lowest alkali consumption occurs at the highest tolerable bisulfite con-

TABLE 1. CHEMISTRY OF SULFUR DIOXIDE REMOVAL

Absorption

$SO_2 + H_2O \rightarrow H_2SO_3$
$SO_2 + NaOH \rightarrow NaHSO_3$
$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O$
$2SO_2 + H_2O + Na_2CO_3 \rightarrow 2NaHSO_3 + CO_2$
$SO_2 + Na_2CO_3 \rightarrow Na_2SO_3 + CO_2$
$SO_2 + H_2O + Na_2SO_3 \rightarrow 2NaHSO_3$

Oxidation

$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

Chemical Addition

$NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O$
$Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + H_2O + CO_2$

Double Alkali Regeneration

$CaO + H_2O + Na_2SO_3 \rightarrow CaSO_3 + 2NaOH$
$CaO + NaHSO_3 \rightarrow CaSO_3 + NaOH$
OR
$Ca(OH)_2 + Na_2SO_3 \rightarrow CaSO_3 + 2NaOH$
$Ca(OH)_2 + NaHSO_3 \rightarrow CaSO_3 + NaOH + H_2O$

centration since only one mole of sodium ion per mole of $SO_2$ absorbed is consumed, compared with 2 moles of sodium ion per mole of $SO_2$ for either sodium sulfite or sodium sulfate.

The various chemical reactions involved in the sodium-based absorption systems for sulfur dioxide are shown in Table 1. It is important to note that the sodium-based solutions can be regenerated in the "double alkali" process using a less expensive calcium alkali to replace the sodium ion and regenerate the sodium ion for re-use in the absorber.

Sodium sulfate formation occurs in all sodium-based absorber systems. Absorber solution temperature, gas phase oxygen concentration, and liquid phase oxygen solubility determination sulfate formation rates. Sulfite is an extremely good oxygen scavenger, and the higher the temperature in solution, the higher the reaction rate. Because sulfate formation is a relatively uneconomic use of sodium ion in an absorption system, and because the sulfate is regenerable only to a limited extent in double alkali systems, everything possible must be done to reduce the incoming gas temperature to the absorber so that the adiabatic saturation temperature in the absorber will be at the lowest possible level. Oxygen concentration can be controlled to a limited extent by operating the boiler with minimal excess air. However, in some industrial stroker-fired coal boilers, oxygen levels simply cannot be reduced without causing large increases in particulate emissions and incomplete fuel combustion. The greatest deterrent to sulfate formation by oxidation of the sulfite is solution chemistry adjustment to limit oxygen solubility. First, high ionic strengths are favored (high dissolved solids levels). Second, high sulfate concentrations, relative to sulfite and bisulfite concentrations, result in the "common ion effect," which limits oxygen solubility by limiting the rate at which sulfate can be formed.

Sodium hydroxide or sodium carbonate consumptions can be significantly reduced by staging the absorption process. In general, the more stages used, the lower the chemical consumption. Staging means the use of different composition absorber solutions in series operated absorption steps, while taking blowdown (or waste liquid) from one step and using it as feed to the preceding absorption step. Scrubbing liquid is used countercurrently in the absorption step to the gas being cleaned in the absorbers. It is possible, using as many as five stages, to achieve outlet sulfur dioxide concentrations of less than 0.1 ppm (vol) with alkali consumptions as low as 1.1 mole $Na^+$ per mole $SO_2$ removed. This can be done with incoming $SO_2$ concentrations as high as 20,000 ppm (vol). In almost all cases, however, two-stage operation is adequate for amine absorption processes used for $CO_2$ production. Incoming $SO_2$ concentrations of up to 3,000 ppm (vol) can be reduced to 1 ppm (vol) with alkali consumptions as low as 1.3 mole $Na^+$ per mole $SO_2$ absorbed. Compared with an average 1.5 to 1.6 mole $Na^+$ per mole $SO_2$ removed in single-stage processes, significant cost savings result.

## SYSTEM OPERATION

In the two-stage systems, the flue gas is brought into contact with a slightly acidic scrubbing solution containing sodium bisulfite, sodium sulfate, sulfurous acid, and sodium sulfite. No free alkali is present in this first absorbing solution. pH levels of 4-6 are common in this stage. The lower the pH, the lower the caustic consumption. Because the absorption solution is acidic, sulfur dioxide partial pressure over the scrubbing solution typically falls between 200 and 500 ppm (vol). The outlet sulfur dioxide concentrations from the first stage typically reach between 250 and 550 ppm (vol). The liquid from the first stage absorber is taken to disposal or regeneration, and the gas from the first stage is taken to the second stage absorber. The liquid, because of its relatively high $SO_2$ partial pressure, should be discharged into a more alkaline environment to reduce the sulfur dioxide partial pressure. Where coal is used as fuel in the boiler, alkalinity in the fly ash, in the form of calcium oxide, is the most common neutralizing agent.

In the second stage absorber, the sulfur dioxide concentration is taken to 1 ppm (vol) or less using a scrubbing solution with a pH of approximately 7. Most of this absorbed sulfur dioxide forms as sulfite and, because of the very low concentration of sulfur dioxide absorbed into this solution, the partial pressure for $SO_2$ is extremely low, typically less than 0.1 ppm (vol). Because of the very small quantity of $SO_2$ removed (on a total mass basis), this stage is considered the "polishing" stage. A schematic flowsheet for an acid gas absorption process preceding a $CO_2$ absorption system is shown in Figure 1. It is interesting to note in this flowsheet that the sodium alkali is added in both stages, rather than being added in its entirety in the second stage. If it is added only in the second stage, some $CO_2$ absorption occurs and the blowdown to the first stage is alkaline. As the liquid is then advanced from the second stage to the first stage, this $CO_2$ is desorbed so that there is no net change in $CO_2$ concentration. Thus, one immediately questions why two separate pH control systems are necessary since the same caustic consumption would result, even if the second stage pH were allowed to be higher with all of the sodium hydroxide or sodium carbonate flowing through it. The reason becomes obvious when one operates a system of this type for any length of time under real plant operating conditions. Fly ash from both coal and

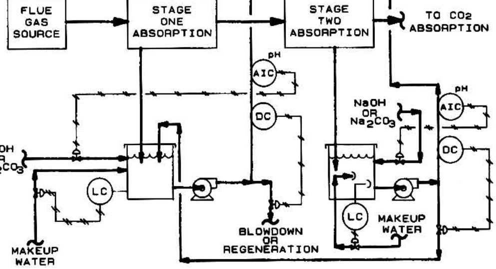


Figure 1. Schematic process flowsheet for two stage sulfur dioxide absorption system.

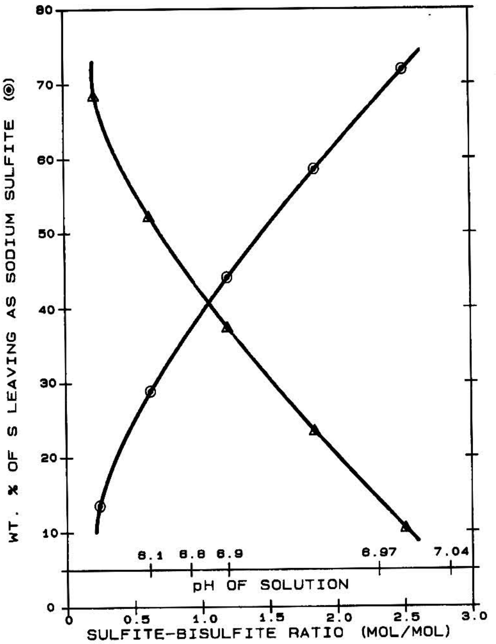


Figure 2. Sulfur distribution in effluent from $SO_2$ scrubbing system when 20% converts to sulfate (% of S leaving as sulfite and bisulfite).

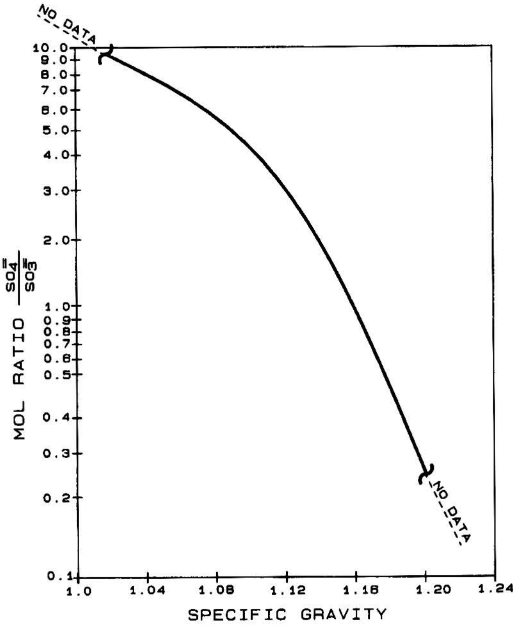


Figure 3. $SO_3^=$-$SO_4^=$MOL ratios at approximately constant pH of 6.7 −6.9 and at temperature of 132°F-141°F.

oil-fired boilers typically contains calcium in the form of the oxide. Most scrubber make-up water has at least some calcium content in the form of water hardness. Combining makeup water calcium and fly ash calcium in an alkaline environment causes formation of calcium sulfite and calcium sulfate (gypsum). These create severe scale formation problems in nozzles, pipes, pumps, tanks, and mist eliminators. To prevent this, if the solutions are main-

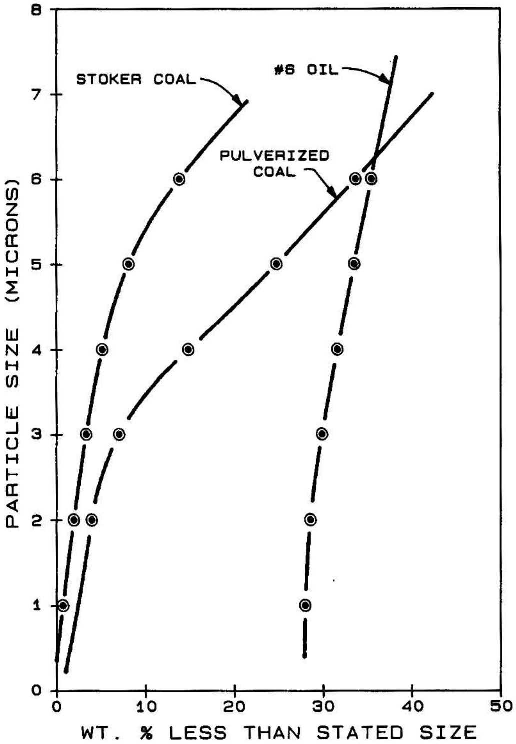


Figure 4. Particle size distributions for stack gas flyash from boilers.

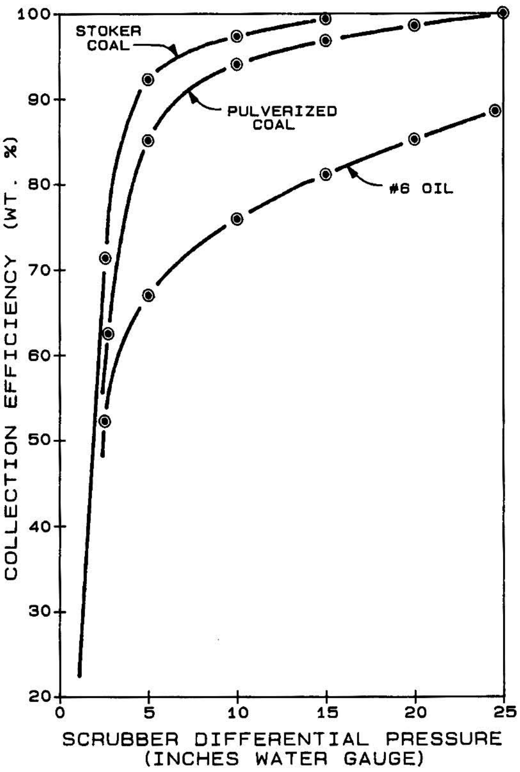


Figure 5. Scrubber performance on boiler flyash emissions.

tained at pH 7 or even slightly less, there may be a 0.3 to 0.5 ppm (vol) $SO_2$ penalty in the outlet gas stream paid, but the reduction in long-term maintenance greatly exceeds the resultant amine consumption and cost of this trace increase in outlet sulfur dioxide concentration. Thus, it is preferred to use two separate pH control systems and distribute the sodium alkali accordingly.

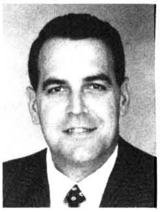
To design a system of this type, it is essential that chemical equilibria data be available for the specific application. These data are developed empirically in laboratory and pilot testing, and are then refined in commercial installations. Chemistry in the absorbers must be controlled precisely with both pH controllers and with conductivity or density controllers to maintain near constant absorptive capacity with the somewhat varied acid gas concentrations encountered in boiler operations of this type. Some of the chemical equilibria data are provided in Figures 2 and 3. Materials of construction become extremely critical in the acidic stage of the two-stage absorber, since most of the boiler fuels have chlorides present and acidic chlorides attack the less expensive stainless steel alloys (Type 304 and 316). The higher nickel alloys must be used to resist this chloride attack.

## PARTICULATE REMOVAL

When scrubbing systems are used for acid gas absorption preceding $CO_2$ absorption systems, the scrubbers can be used to reduce particulate concentration from the boiler flue gas. Obviously, natural gas combustion would be preferred since it generates almost no particulate matter and almost no acid gas to be removed. When coal is used as the fuel, two distinctly different particle size distribution fly ash products are produced. The larger size distribution material is produced by a stoker-fired boiler, where most of the ash remains in the furnace. The smallest size distribution ash is produced by pulverized coal boilers. When oil is fired as the fuel, the particle size distribution is substantially smaller than for any type of coal firing. Comparative size distributions are shown in Figure 4. Scrubber performance, as a function of scrubber differential pressure on all of these fly ash types, is shown in Figure 5.

## OTHER ACID GASES

With regard to $NO_x$, there is no economic scrubbing technique available using either oxidative or reductive chemistry. The nitrogen oxide reductions typically occur in the boiler itself, using ammonia catalyzed reduction, selective catalytic reduction over precious metals catalysts, or combustion modification techniques which reduce peak flame temperatures and thus reduce production of $NO_x$. None of these techniques, however, produce $NO_x$ concentrations less than about 80 ppm (vol) in the exhaust gas from the boiler and scrubbing system. $SO_3$ and $H_2SO_4$ aerosol emissions are reduced somewhat (typically between 30 and 40% in conventional scrubbing systems). If higher removal efficiencies are required, relatively high differential pressure aerosol filters must be used, or wet electrostatic precipitators can be considered. These are typically add-on systems following the sulfur dioxide absorbers. HCl, HF, HI, and HBr removal occurs at very high removal efficiency in these systems producing the soluble sodium salts of the halides.



**Jack D. Brady** holds a B.S. degree in Chemistry from San Jose State University. He became active in the pollution control field in the mid-1960's when he formed Pacific Technical Services, a company specializing in engineering and manufacturing of air pollution control equipment, headquartered in Santa Rosa, California. In 1971, Pacific Technical Services was sold to FMC Corporation and became FMC's Air Pollution Control Operation. He managed this operation for FMC until early 1975 when he joined Andersen 2000 Inc. as Executive Vice President and became President in early 1978. He holds more than twenty U.S. patents and more than 100 international patents on air and water pollution control equipment and heat recovery systems, has authored three books on air pollution control and has presented papers and seminars before many scientific societies.

# RCRA Trial Burn Considerations

**James J. Cudahy and Thomas G. Busmann**

IT Corporation, Knoxville, TN 37923

*The new Resource Conservation and Recovery Act (RCRA) hazardous waste incineration regulations have ushered in a new era which will result in a better understanding of the significant combustion design parameters relative to hazardous waste destruction. This paper discusses some of the important issues involved with the RCRA trial burn program, RCRA trial burn database information, and three RCRA research trial burn programs. These programs have made significant contributions to an increased understanding of important incineration destruction and emission mechanisms.*

## INTRODUCTION

The publication of the first RCRA incineration regulations in December 1978 brought industrial incineration from a qualitative study of black smoke, ash and carbon monoxide to a new and relatively unknown quantitative area of destruction and removal efficiency (DRE). The new RCRA DRE performance standard has been one of the most significant occurrences in the history of industrial incineration, because the regulations will eventually lead through research to a better understanding of the fundamental physical and chemical processes taking place in the incineration process.

It is now over eight years since the publication of the EPA's first proposed set of hazardous waste incineration (HWI) regulations in December 1978 [*1*]. These proposed regulations, which included the concept of a trial burn, were followed by interim final HWI regulations in January 1981, [2] and interim final amendments in June 1982 [3]. The purpose of this paper is to discuss the RCRA trial burn program relative to current status, existing technical issues, and trial burn testing results.

## CURRENT TRIAL BURN PROGRAM STATUS

Early estimates of the number of incinerators capable of handling hazardous wastes (HW) were as high as 340 [4]. Industry, through a program of delisting, exemptions, source control, boiler usage, and incinerator shut-downs, apparently has reduced the number of RCRA HWIs to below 340. A recent EPA RCRA incineration summary states that 224 HWI Part Bs have been called and 139 trial burn plans received [5]. It is not known if these numbers include calls from states with RCRA primacy. As of April 30, 1985, there had been 18 trial burn permits issued, 5 denied, and 42 closures or HWIs that became nonregulated [5].

It is very difficult at this time to obtain current information on RCRA trial burns. To obtain current RCRA HWI test results it is necessary to contact the Freedom of Information Officer in each region, which is a complicated and difficult process.

It is not known how fast RCRA trial burn plans are being processed. However, early results have been slower than anticipated. Two trial burn plans prepared by IT Corporation for interim status liquid incineration systems were submitted to Region IX in August 1983 and to Region II in January 1984. A Notice of Deficiency (NOD) was received 15 months later from Region II, and 16 months after trial burn plan submittal for the Region IX unit.

## MAJOR TRIAL BURN TECHNICAL ISSUES

This section will concentrate on some of the major technical issues that the authors have identified during the preparation of about 20 RCRA trial burn plans for industrial and governmental clients.

### Principal Organic Hazardous Constituents (POHCs)

POHCs have historically received the most attention and publicity from the incineration community; however, the initial results from the RCRA trial burn program are indicating that well-designed incinerators, boilers, and other thermal systems are typically able to meet the 99.99 percent destruction removal efficiency (DRE) performance standard.

A major problem with the current POHC/DRE situation centers on the EPA's insistence on the use of more than one POHC during a RCRA trial burn. The problem occurs because the EPA has established an incinerability hierarchy which ranks the Appendix VIII constituents supposedly according to difficulty of incinerability.

This incinerability ranking is based on the heat of combustion of each Appendix VIII constituent. In the EPA heat of combustion model, the thermal stability is inversely proportional to the heat of combustion. The higher the heat of combustion, the lower the thermal stability of the Appendix VIII constituent. The EPA regulations, and the EPA Guidance Manual for Hazardous Waste Incinerator Permits, assume a perfect correlation between thermal stability and inverse heat of combustion [6]. The regulations and Guidance Manual use the Incinerability Ranking to decide which Appendix VIII constituents can be incinerated under a RCRA Permit and which cannot. According to the Guidance Manual, the highest ranking Appendix VIII constituent (POHC) destroyed during the trial burn at the >99.99 percent level becomes the permit benchmark. The only Appendix VIII constituents that can then be permitted for incineration are those on the Incinerability Ranking List that are equal to or below the highest ranking trial burn POHC which had a >99.99 percent DRE [6].

The EPA admits, however, in the Guidance Manual that the Incinerability Ranking according to heat of combustion is approximate [6]. Vapor phase and theoretical thermal oxidation work by the University of Dayton and others, [7, 8, 9] has shown poor correspondence of the heat of combustion ranking list and actual thermal stability for Appendix VIII constituents and other compounds. The University of Dayton work is probably the best source of Appendix VIII thermal stability data [9]. Though limited in the number of compounds evaluated, the Dayton work allows much more realistic thermal stability ranking of Appendix VIII constituents than the heat of combustion model. Cudahy, et al., published a list of about 55 chemical compounds ranked according to vapor phase thermal stability [*10*].

The number of POHCs selected for the trial burn is negotiated between the incinerator owner/operator and the EPA or state agency. The EPA has stated that more than one POHC should be selected and should be limited to no more than six overall [6]. Since the number of POHCs greatly affects the trial burn sampling and analytical costs, the negotiation of the number of POHCs should not be taken lightly.

The negotiated number of POHCs should be kept as low as possible, and should be limited to only one. This one POHC should be a compound with a high thermal stability according to both heat of combustion and vapor phase data. The negotiation of only one POHC is very important because at the present time there are no EPA regulations, guidelines, or strategies to cover a situation where an incinerator passes the DRE test for a high ranking, low heat of combustion, low stability compound like chloroform but does not pass for a low ranking, high heat of combustion, relatively high stability compound like toluene. Because there are no EPA regulations to cover this situation and since toluene is last on the EPA's ranking list, the incinerator might not be permitted, and the permittee could possibly be required to perform another expensive RCRA trial burn. Therefore, in order to have a trial burn that can be meaningfully evaluated, only one Appendix VIII constituent should be selected during the negotiation process for each physical state of waste incinerated.

There are indications that the EPA will accept only one POHC. At a meeting in November 1985, EPA Region II authorities accepted a trial burn plan with only one high ranking ($CCl_4$) POHC.

### Non-Chlorinated POHC Selection

The selection of a high ranking POHC for those systems without HCl removal capability is not an easy process. Most of the high ranking Appendix VIII constituents on the EPA's Incinerability Ranking List are highly chlorinated compounds. Most of the highest ranking non-chlorinated Appendix VIIIs are generally unsuitable because method development will be required to analyze these compounds at the low levels expected in an incineration stack gas. Formic acid, formaldehyde and phenol are examples which probably cannot be analyzed adequately in a stack gas at ppb levels using SW-846 methods.

A possible solution to this problem would be to select a high ranking and thermally stable chlorinated Appendix VIII compound and negotiate to allow the incineration of this chlorinated compound only during the trial burn. Successful incineration of this high ranking Appendix VIII constituent during the trial burn therefore results in a high degree of DRE permit flexibility to incinerate new non-halogenated wastes without the need to do another trial burn.

### Combustion Gas Velocity Indicator (CGVI)

The RCRA regulations specify that an appropriate indicator of combustion gas velocity must be measured during the trial burn, specified as a permit condition, monitored during permitted operation, and used as a waste feed cut-off parameter.

This CGVI permit condition sounds simple to implement; however, it is a complicated technical flow measurement problem. The selection of the best CGVI monitoring system will depend on the type of incinerator, the type of prime mover (forced draft or induced draft), whether water injection is practiced, and the CGVI location. If located after a wet scrubbing system, the CGVI flow measurement system has to operate in a situation with condensing moisture which is typically corrosive. If located before a wet scrubbing system, the CGVI flow measurement system has to operate in a hot, particulate-laden gas at temperatures that could range from about 500 to 2200°F (260 to 1200°C) or higher. Design of a reliable, low maintenance flow measurement system under these conditions is not easy. It is recommended that various CGVI systems be evaluated in the operating incineration system prior to the RCRA trial burn in order to select the best and most practical CGVI system for each incinerator. IT is currently evaluating as CGVIs, the use of an annubar, dp cells used with low $\Delta p$ stack restrictions, and a stack insert which measures a temperature difference between two rods which is proportional to the stack gas flow.

### Carbon Monoxide (CO) Monitoring

The RCRA HWI regulations require that each permitted system include a continuous CO monitor which will be used to automatically cut off the waste feed when CO levels exceed permitted maximum levels. The permitted maximum allowable CO levels are negotiated values which are supposed to be based on CO levels during the RCRA trial burn. The EPA's original purpose of the CO monitoring/cut-off system was based on the assumption that high CO levels would indicate high POHC emissions and therefore lower DREs. Unfortunately, this does not seem to be a valid assumption. Seeker, et al., in a recent EPA-sponsored project using a small, turbulent flame reactor, showed that a substantial change in CO levels could occur before the exhaust concentration of waste compounds increased significantly [*11*].

The study also found that there was a reasonable correlation between destruction efficiency (DE) and total hydrocarbon (THC) or methane emission levels as measured by a flame detector (THC) or an NDIR analyzer ($CH_4$).

Other EPA HWI studies at the Eleventh Annual EPA Research Symposium held in Cincinnati in April 1985 also concluded that CO emission levels can get quite high before the DRE starts to decrease significantly.

Another recent paper by Daniels looks at CO emission levels from both a theoretical aspect and also using real-world considerations involved with the incineration of solid wastes [*12*]. The paper points out that even with secondary combustion, the incineration of solid wastes can result in CO "spikes." CO spikes are short-term transients that can reach levels of 1000 ppm or higher for a brief duration. The authors conclude that these CO spikes are not indicative of significant DRE deterioration and suggest that EPA permit writers allow for normal CO variation when specifying CO permit limits in order to protect against unnecessary activation of the CO/waste feed cut-off system. The authors suggest that hourly average or daily average CO be used as a permit condition rather than an instantaneous CO level.

Another possibility which has been used by IT in its trial burn plans involves the use of a timer and a two-tier waste feed cut-off system. CO spikes above the first CO permit level would start a timer. If the CO stays above this permitted level for a certain period of time, the waste feed would automatically cut off. If the second higher CO permit level is exceeded, the waste feed would immediately cut off. In West Virginia, Region III of the EPA has accepted this approach on a liquid HWI [*13*]. Another practical solution involves the use of a time weighted average CO value as a permit condition. This approach has been negotiated as a permit condition for a HWI located in Texas.

Other important CO monitoring considerations for any company planning a RCRA trial burn are the following:

1. Install, calibrate, and debug the CO monitoring system before the trial burn.
2. Before the trial burn, develop and document the day-to-day normal CO level variations for use during permit negotiations.
3. Discuss with the state and EPA how long your HWI will be allowed to operate if your CO monitor is down for maintenance. Will you need a spare CO monitor?

Relative to the EPA work on CO and THCs, it is hoped that the EPA will carefully consider and research the real-world implications of this work. Does THC monitoring correlate with DRE in full-scale systems? Is THC monitoring practical and can it be done continuously at reasonable maintenance levels? A study done by Midwest Research Institute on eight full-scale HWI systems concludes that THC may not be a good predictor of DRE changes. That study is discussed in a later section of this paper.

#### Ash Spiking

In order to obtain a flexible permit relative to the ash content of the organic and aqueous waste liquids being incinerated, the trial burn waste liquid should be spiked with an ash surrogate to a higher ash level than is normally encountered. This is another seemingly simple concept that is difficult to implement in the real world. The EPA Guidance Manual suggests the use of either incinerator flyash, coal ash, diatomaceous earth, powdered gypsum or limestone [6]. All of these materials, however, will require suspension in the liquid waste and can cause plugging in feed lines and burner nozzles during the trial burn. Pretrial burn testing in this area is strongly recommended to develop a practical ash surrogate system which is agreeable to the EPA and will provide a flexible ash content permit condition.

#### Continuous Solids Waste Feed Rate

The RCRA HWI regulations and Guidance Manual were written primarily for liquid wastes, even though they are supposed to cover both liquid and solid wastes. The regulations [40 CFR 264.347(a)(1)] require continuous monitoring for waste feed rate. This is difficult to accomplish when various solids such as trash, fiber packs, steel drums, and sludges are being fed to the incinerator by various methods such as crane, conveyor, ram feed, front end loader, and sludge pump. Coming up with an inexpensive, practical solids monitoring system that will be acceptable to the EPA must be carefully thought out before entering trial burn negotiations.

#### Different State and Federal Regulations

While many states have identical or equivalent RCRA HWI regulations, others, like New Jersey, have HWI regulations that are significantly different, more stringent and have to be considered during trial burn preparation. New Jersey's particulate emission limit, for example, is 0.03 grains per dry standard cubic foot corrected to 7 percent $O_2$ instead of RCRA's 0.08 grains.

Other states such as California have developed incineration related guidelines under the Air Toxics Division which are stricter than RCRA and will need to be considered when developing a trial burn plan and negotiating an incineration permit [*14*].

### PRE-TRIAL BURN TESTING

A HWI owner/operator should never go into a RCRA trial burn without having a good idea of what the incinerator's capabilities are. A pre-testing program should be designed and implemented using inexpensive sampling and analytical techniques such as THC monitoring, single VOST tests, and Method 5 particulate and HCl sampling to define the capabilities of the incinerator. This concept is discussed in detail by Peters in a recent paper which described three pretrial "mini-burns" [*15*].

### TRIAL BURN DATABASE

The EPA originally started to develop a HWI database under Dr. C. C. Lee (EPA/Cincinnati), but because of funding problems this important activity has been dropped. Recently Oak Ridge National Laboratories (ORNL) in Oak Ridge, Tennessee received funding to continue development of this database, but as of June 1985 has not yet started conversion of the database to the ORNL computer system.

The EPA has funded a RCRA trial burn database book which is soon to be published. A recent paper discussed this book and gave summaries of data from RCRA or simulated RCRA trial burns in 23 HWIs, eleven lime, cement, and aggregate kilns, and nine industrial boilers [*16*].

An active up-to-date database of this kind is important since it may someday reduce the need for expensive DRE testing on similar incinerators. It should also reduce the need for costly negotiating sessions involved with having to document to the EPA why a new commercially proven McGill, John Zink, or Trane HWI is designed properly.

#### Number of RCRA Trial Burns Completed

As of June 1985, the previously mentioned IT HWI database survey had identified at least 14 trial burns which had been conducted. This number does not include results from EPA Regions II, VI and X, nor does it include EPA research and industrial research studies such as the three described in the following section. Table 1 summarizes the trial burn locations that IT has been able to identify through June 1985. This is not intended to be a comprehensive list.

### RESEARCH TRIAL BURNS

Because the regulatory DRE concept is relatively new and DRE stack gas analytical techniques are still in the development stage, early full-scale work focused mainly on DRE data. Three trial burn reports which are informative and shed some light on the attainability of the 99.99 percent DRE and the other RCRA performance standards are summarized in this section.

#### MSD Incinerator Trial Burn

The MSD incinerator in Cincinnati was the site of perhaps the first full-scale RCRA trial burns in July and September 1981. The trial burns were funded by the EPA to verify the EPA's RCRA HW trial burn sampling and analytical protocols and recommended procedures [*17*].

The MSD incinerator is a rotary kiln followed by a fired

TABLE 1. PARTIAL LIST OF RCRA TRIAL BURNS CONDUCTED THROUGH JUNE 1985

| Owner | Location | Type Incinerator<br>RK[a] | LIQ[b] | FB[c] |
|---|---|---|---|---|
| USEPA-ORD/EERU | Edison, NJ | X | | |
| Dupont | Martinsburg, WV | | X | |
| Dupont | Wilmington, DE | | X | |
| Gulf Oil | Philadelphia, PA | | | X |
| Smith-Kline | Conshohocken, PA | | X | |
| Union Carbide | S. Charleston, WV | | X | |
| CIBA-GEIGY | McIntosh, AL | X | | |
| Olin Chemical | Brandenburg, KY | | | |
| Pennwalt | Calvert City, KY | | X | |
| SCA/Waste Management | Chicago, IL | X | | |
| ENSCO | El Dorado, AR | X | | |
| McDonnell Douglas | St. Louis, MO | | | |
| MOBAY | Kansas City, MO | | | |
| USEPA-ORD/EERU | McDowell, MO | X | | |

[a] Rotary kiln.
[b] Liquid injection.
[c] Fluidized bed.

secondary combustion chamber. Liquid wastes containing eleven different POHCs were fed to the rotary kiln and the secondary combustion chamber. The following eleven POHCs were used:

Chloroform
Carbon tetrachloride
Hexachloroethane
Hexachlorobenzene
Hexachlorocyclopentadiene
Trichloroethane
Tetrachlorethane
Bromodichloromethane
Pentachloroethane

During the nine tests, secondary combustion chamber temperatures varied from 899°C (1650°F) to 1316°C (2400°F) and secondary combustion chamber residence times varied from 1.5 to 3.7 seconds. The rotary kiln temperature and residence times are not included in these values. Almost all the DREs obtained were 99.99 percent or greater. There was only one test where the 99.99 percent was clearly not achieved. During this test a DRE of 99.97 percent was obtained for bromodichloromethane at 899°C and 2.3 seconds. At 1316°C and 1.5 seconds, however, the bromodichloromethane had a DRE of 99.995 percent.

The wastes that were incinerated contained water at concentrations ranging from 4.65 to 65.3 percent. As can be seen from the list of wastes, all the POHCs were low aqueous solubility, high volatility POHCs which would tend to volatilize rapidly from aqueous droplets formed during the waste atomization. It is important to get the POHC into the vapor phase as quickly as possible to maximize its temperature, residence time, and oxygen contact. The next trial burn clearly illustrates this concept.

### Eastman Kodak (EK) Trial Burn

The Eastman Kodak Company in Rochester, New York, as part of an internal research project, conducted extensive DRE testing in its 96 GJ/hour (90 MM Btu/hour) rotary kiln (RK) secondary combustion chamber (SCC) incinerator [*18*]. Wastes were fed to the RK or the SCC at temperatures ranging from 704 to 1010°C (1300 to 1850°F) and residence times from 1.2 to 3.3 seconds. Two waste mixtures were used, one with 40 percent water and 13,945 J/gram (6,000 Btu/pound) and another with 18 percent water and 23,244 J/gram (10,000 Btu/pound). A total of nine POHCs were examined. The study attempted to determine the impact on DRE of the following parameters:

Bulk gas temperature
Residence time
Heat content of waste mixture
Heat of combustion of POHCs
Autoignition temperature
Aqueous solubility of POHCs

EK concluded that several factors affected the POHC DREs. Kiln fed POHCs that had longer residence times than SCC fed POHCs had higher DREs. Waste mixtures with higher heat contents had higher DREs. Increasing the RK temperature from 704 to 871°C (1300 to 1600°F) caused higher DREs, but a further increase to 1010°C (1850°F) caused no significant change in DREs. Finally, EK found that water-soluble compounds in aqueous wastes had lower DREs than water-insoluble compounds. The data compiled is listed in Table 2.

As can be seen from these data, the DREs are apparently related to the compound's aqueous solubility which is indicative of the compound's volatility in the aqueous phase.

Since highly water-soluble organics typically have low volatility in aqueous solutions and since atomized water droplets tend to be larger and take longer to evaporate than organic droplets, the highly soluble organic present in the aqueous droplets takes longer to volatilize and be subjected to the combustion conditions. High solubility organics in aqueous wastes will therefore probably require careful design attention to atomization, droplet size, nozzle type, droplet evaporation rate, extended residence time considerations, and possibly waste preheating outside the burner assembly [*19*].

### Midwest Research Institute (MRI) Study

The MRI study was a simulated RCRA evaluation of the baseline performance of eight full-scale incineration systems with various air pollution control systems [*20*]. RCRA DRE, particulate and HCl emissions were measured for the eight HWIs. The study also evaluated products of incomplete combustion (PIC) and specific metal emissions. Rotary kilns, liquid injection and two-chamber pyrolytic and oxidative systems were evaluated. Among the conclusions were the following:

1. DREs were generally equal to or greater than 99.99 percent.
2. The only clearcut relationship that could be correlated with DRE was the POHC feed concentration. The higher the POHC feed concentration, the higher the DRE.
3. POHC levels in ash and scrubber water were generally very low or nondetectable.
4. POHCs and/or PICs such as trihalomethanes can enter the stack gas at significant levels by being stripped from the scrubbing water in the APC equipment.

TABLE 2. THE DESTRUCTION AND REMOVAL EFFICIENCY, (DRE) AND AQUEOUS SOLUBILITY OF NINE COMPOUNDS

| Compound | Solubility (wt%) | DRE |
|---|---|---|
| Heptane | 0.005 | >99.995 |
| Hexane | 0.010 | >99.995 |
| Chloroform | 0.80 | >99.995 |
| Methylene chloride | 2.0 | >99.995 |
| Acetone | Completely | 99.99 |
| Isopropanol | Completely | 99.99 |
| Ethanol | Completely | 99.88 |
| Methanol | Completely | 99.83 |
| 1,4-Diethylene dioxide | Completely | 99.60 |

5. PICs were generally at low levels in the stack gas and could come from other sources such as the feed or the scrubbing water.
6. Compliance with the RCRA particulate emission performance standard was only achieved at about half of the sites tested.
7. THC and CO were monitored on a continuous basis and did not appear to be good predictors of either POHC emissions or DRE.
8. The RCRA HCl performance standard was generally achieved.
9. Contamination of the POHC/PIC stack gas sampling tubes from the ambient air prior to testing can be a significant problem and must be carefully controlled.

MRI attempted to develop correlations based on all the HWI data for DREs and various incineration parameters such as temperature, residence time and heat of combustion. The only parameter, however, that showed a good correlation with DRE was the POHC feed concentration. MRI stated that the prediction of DRE performance based on evaluation of commonly measured operating or design parameters may not be reasonable [*20*].

This lack of correlation between DRE and the traditional incineration parameters occurred because MRI was comparing apples and oranges. It is the author's opinion that DRE data cannot be compared for different pilot and/or full-scale systems. Factors such as flame temperatures, liquid matrix-waste constituent vapor-liquid equilibria, mixing/turbulence, different burner designs, solid matrix-constituent evaporation rates and localized pyrolysis all result in DRE comparisons for different incinerators being essentially meaningless. The important fact is that the 99.99 percent DREs are being achieved in almost all HWI systems tested.

## SUMMARY

The new RCRA HW incineration regulations have ushered in a new era which will result in a better understanding of the significant combustion design parameters relative to HW destruction. This paper has discussed some of the important issues involved with the RCRA trial burn program, the important RCRA HWI databases, and three RCRA research trial burn programs which have made significant contributions to an increased understanding of important HWI destruction and emission mechanisms.

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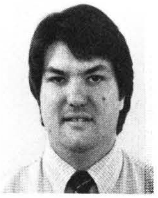
**James J. Cudahy** is Manager of Business Development for Thermal Treatment for the IT Corporation in Knoxville, TN. He is responsible for fixed hazardous waste incineration and on-site thermal treatment systems. He earned a B.S.Ch.E. at Newark College of Engineering, an M.S.Ch.E. at the University of Delaware and an MBA from Michigan State University in 1968. He has 15 years experience in hazardous waste incineration design and permitting and has over 25 related presentations and publications. He is a registered professional engineer in Tennessee, Michigan, and Louisiana.



**Thomas G. Busmann** is a Project Engineer in the Process Engineering group with IT Corporation in Knoxville, Tennessee. He is involved in design, operation, and permitting of incineration and hazardous waste processing facilities. He earned a B.S.Ch.E. from the University of Idaho in 1980. He is a member of AIChE and is an EIT in Idaho.

# Modeling the Adsorption of Target Compounds by GAC in the Presence of Background Dissolved Organic Matter

**Edward H. Smith, Szu-Kung Tseng, and Walter J. Weber, Jr.**
Environmental Engineering Program, The University of Michigan, Ann Arbor, MI 48109

*The impact of background dissolved organic matter (DOM) on the adsorption of a target organic compound, lindane, by GAC was examined. Both capacity and rate of lindane removal decreased in proportion to the DOM concentration. Two modeling approaches employing homogeneous surface diffusion versions of the Michigan Adsorption Design and Applications Model (MADAM-HSD) adequately simulated and predicted data for fixed-bed adsorbers. In one approach, adsorption equilibrium and mass transport parameters were evaluated and the data modeled in terms of the target compound only, using a single-solute modeling scheme. The second methodology treated the background DOM as an independent component and utilized a two-solute version of MADAM-HSD to describe and/or predict adsorber breakthrough profiles for both lindane and DOM. The short bed adsorber (SBA) technique was verified as a useful tool for determination of the mass transport parameters associated with the systems studied.*

## INTRODUCTION

Granular activated carbon (GAC) adsorption in fixed-beds is recognized as one of the fundamental treatment technologies for waters and wastewaters contaminated with potentially hazardous organic compounds. The site to site variability and complex composition of many waters and wastes, however, complicate the design and operation of carbon adsorption treatment processes. In addition to anthropogenic organic contaminants, naturally occurring organics, usually referred to generically as humic substances, are commonly present, often at relatively high concentrations. Although treatment objectives may be directed toward a specific target compound (or compounds), the transformations and interactions occurring among species in solution cannot be ignored if the adsorption process is to be properly appraised. For instance, a target organic compound in a system containing activated carbon and background dissolved organic matter (DOM—e.g. humic material) can exist in one or more of at least four states: 1) free, in solution; 2) bound to the humics, in solution; 3) adsorbed to the activated carbon; or 4) bound to an adsorbed humic molecule. It is likely that all four states exist in interactive equilibria, with the net distribution being dependent upon the kinetics and degree of reversibility of the reactions.

A substantial body of adsorption data and analysis exists for the individual interactions described above. Numerous researchers have investigated the removal of humic substances by activated carbon under a variety of conditions [*1-3*]. The literature is replete with research reports on single and multicomponent adsorption of specific organic compounds onto activated carbon (for a review, see reference [*4*]. To date, only a few studies have combined these systems to investigate the adsorption of organic substances under conditions more closely approximating those in the field [*5-11*]. Several general observations have derived from these studies: 1) the presence of background organic matter in solution can alter adsorption capacities and rates of target compounds, with the impact being variable for different classes of organic compounds; 2) monitoring of organics may be functionally achieved in certain treatment applications by measuring a collective surrogate parameter such as total organic carbon (TOC), dissolved organic carbon (DOC), total organic halogen (TOX), ultraviolet absorbence (UVA) or a weakly-adsorbing tracer compound; and, 3) existing mathematical models and approaches can be modified to describe the adsorption process for complex mixtures of organics.

This last point is one of the most challenging areas in current research and development of field applications of adsorption technology. In one approach, adsorption data are modeled in terms of the target organic compound(s) only, treating other compounds such as humic material as an unspecified but system-specific background, and experimentally evaluating all model rate and equilibrium parameters for the target compound in the presence of that particular background [*5*, *6*]. Other investigators have attempted a more general approach by combining all organics into a single lumped parameter such as TOC, DOC, or TOX [*7-10*], and modeling the behavior of that parameter. A related methodology involves treating the background substance as a single component in addition to the target compound(s) and employing multicomponent models for analysis. In an extension of this approach, the lumped parameter characterization of the background water is broken down into a number of pseudo-species whose individual isotherm properties are hypothesized from lumped parameter data and Ideal Adsorbed Solution (IAS) theory [*7*]. The parameters of these pseudo-species can then be used for predicting adsorption equilibria for specific target compounds in the presence of the given background water. It is hoped that this technique can more accurately quantify the adsorptive properties and impacts of various types of DOM, although the method is virtually untested for rate parameters. Using this idea, another approach has evolved in which several pseudo-components are postulated for the unknown mixture. To determine the isotherm properties of these theoretical components, a weakly-adsorbing tracer compound is either added to or singled out in the mixture, and the theoretical component parameters computed by matching the displacement of the tracer compound from its single solute isotherm [11]. A related effort utilizes species grouping, i.e. reducing a multicomponent solution to a system of a fewer number of pseudo-species characterized by "average" adsorption parameters, hence simplifying multicomponent equilibrium calculations [12].

Predictive mathematical models have been established as useful tools for estimating the breakthrough or pattern of appearance of adsorbing solute(s) in the effluent from fixed-bed adsorbers as a function of time or volume of water treated. Once properly calibrated for specified influent and operating conditions, such models can be utilized for optimal design and operation of pilot-scale and, eventually, prototype adsorber units. The predictive ability of an adsorption model is predicated on identification and quantification of model input parameters which accurately characterize the operative physical phenomena in an adsorber. Combined film and particle diffusion models have received the most widespread application because they account for the two most common rate-limiting steps, namely film and intraparticle mass transfer. The general approach in such models is numerical solution of the solid and liquid phase material balance expression for the carbon bed coupled by an equation to describe equilibrium phase distribution of the adsorbate. One such model, the homogeneous surface diffusion (HSD) version of the Michigan Adsorption Design and Applications Model (MADAM) [13, 14], requires a film diffusion parameter, $k_f$, a specific intraparticle diffusivity, $D_s$, which is assumed to relate to diffusional transport along the pore surfaces, and appropriate isotherm coefficients to compute the equilibrium liquid phase concentration of solute for a given corresponding solid phase value. Due to the system specificity of these parameters, they are usually measured/calibrated in bench-scale laboratory experiments which attempt to simulate the particular system of interest.

A recent concern in adsorption modeling is the high level of mathematical sophistication of dynamic models versus a questionable analytical certainty of model inputs which must be obtained experimentally. This is particularly true in the case of mass transport parameter evaluations, which have commonly been done by subjecting rate data from completely mixed batch reactor (CMBR) studies to a statistical parameter search to estimate the $k_f'$, (i.e. $k_f$ from CMBR conditions) and the $D_s$ values. Because the hydrodynamic characteristics of a fixed-bed reactor are significantly different, correlation techniques are required to convert $k_f'$, to $k_f$. Associated errors in both search and correlation techniques can result in the compounding of errors having the same direction. Alternative calibrating approaches using specially designed bench-scale apparatus such as the short-bed adsorber (SBA, defined as a bed of sufficiently short length that immediate concentration breakthrough occurs) more closely approximate the hydrodynamics of full-scale columns and thus provide for more rapid, accurate and reliable determination of adsorption parameters (15, 16). The SBA technique allows simultaneous determination of $k_f$ and $D_s$, eliminating error-compounding by mutual compensation of individual errors in $k_f$ and $D_s$ during parameter search/regression analysis. Although employed almost exclusively for cases of target organics in pure solution to date, this tool offers substantial promise for reducing the gap between bench- and field-scale bases for design of carbon adsorbers treating complex mixes of organics.

The primary objectives of this work were to: 1) examine two alternative approaches for fixed-bed adsorber modeling of a target compound in a background water containing DOM; 2) evaluate the predictive capability of models such as MADAM when implemented in variable modeling approaches for complex solutions; and, 3) explore and evaluate the utility of the SBA technique for determination of mass transport parameters for a target compound in background DOM.

## MATERIALS AND METHODS

### Solutes

Lindane (γ-1,2,3,4,5,6 hexachlorocyclohexane), the target compound selected for the study, is a slightly polar chlorinated insecticide of low volatility (Henry's constant = $4.8 \times 10^{-7}$ $M^3$/atm mol) and solubility (7.2 ppm @ 20°C). The log octanol:water partition coefficient is reported as 3.72 [17]. The chlorinated structure and low volatility render lindane a convenient compound for laboratory investigations, while its hydrophobicity and solubility are typical of a variety of hazardous synthetic organic compounds found in the environment. Lindane's highly chlorinated structure also enables electron capture gas chromatography (GC) analysis at rather low detection limits (< 1 ug/l). Hexane extracts were analyzed for lindane using a 1.83-m long, 6.4-mm diameter stainless steel column packed with 10% OV-17 on 60/80 Gas Chrom Q°, and GC injector and oven temperatures of 250°C and 225°C, respectively. Reagent-grade lindane was obtained from Eastman Kodak Company (Rochester, NY).

Background DOM was simulated by a commercial humic acid. Technical-grade dried humic acid was obtained from Aldrich Chemical Company (Milwaukee, WI) and prepared as a concentrated stock solution which could then be diluted to desired levels as mg/l TOC. Ultraviolet spectroscopy at 250 nm (lindane did not absorb at wavelengths in this range) correlated with TOC measurements was selected for quantitative analysis of humic acid concentration.

Experimental solutions were prepared in deionized glass-distilled water with $10^{-3}$ M phosphate buffer at pH 4 or 7. Solution pH was adjusted by addition of 0.1 N NaOH or 0.1 N HCl.

### Activated Carbon

Filtrasorb 400 (F-400, Calgon Corporation, Pittsburgh, PA) commercial GAC was the adsorbent used in all experiments. A carbon sample was sieved and the fraction passing a 40 mesh U.S. standard sieve and retained on a 50 mesh sieve isolated for this study. The selected fraction was then washed with deionized distilled water to remove leachable materials and carbon fines. The carbon was then dried to constant weight at 105°C and immediately desiccated until use.

### Isotherm Studies

Adsorption isotherm experiments were conducted using the CMBR bottle-point technique in which each point on an isotherm is obtained from an independent experiment conducted in one of a series of sealed-bottle CMBR's. A series of 100-ml aliquots of known adsorbate concentration, $C_0$, were added to glass bottles containing accurately weighed amounts of carbon. Several additional bottles containing the same absorbate concentration but no carbon were prepared as control samples. All bottles were sealed and agitated in a specially designed tumbler for eight days at room temperature. At the end of this equilibration period, a sample from each reactor was analyzed for lindane or lindane and humic acid according to the aforementioned analytical procedures. Upon measurement of the equilibrium solute concentration, $C_e$, the corresponding equilibrium solid phase concentration, $q_e$, was calculated according to:

$$q_e = \frac{C_o - C_e}{M} \tag{1}$$

where M is the carbon dose (mass carbon/liquid volume in reactor).

### Fixed-Bed Adsorber Studies

The fixed-bed adsorber studies were divided into two major categories according to adsorber depth. SBA experiments employing a very small adsorber depth (1.3 cm) were utilized to obtain the mass transport parameters for modeling purposes. Deep-bed adsorber (DBA) systems of greater depth (6.5 cm) were then used to collect data to compare to mathematical predictions for model verification.

All of the fixed-bed adsorber studies were conducted with 1-cm (I.D.) glass tubing. The columns were operated in a downflow mode with flow rates of approximately 15 ml/min (194.86 l/m²/min) and a bed void ratio of 0.59. Columns were packed with successive layers of micro-glass beads, GAC, and more beads to establish a consistent flow pattern in and out of the bed. Apart from the factor of length, the DBA column structure and operating parameters and procedures were the same as those for the SBA calibration runs, a necessary requirement for meaningful model calibration and verification.

Due to the rapid initial solute breakthrough in the SBA, more frequent sampling was done during the first hour of the run. SBA tests spanned a 24 to 42 hour duration, while DBA experiments were typically conducted over a period of 100 hours. Upon collection at timed intervals, samples were analyzed for lindane and humic acid and compared to their respective column influent concentrations.

## RESULTS AND DISCUSSION

### Hypothetical Exercise

Figure 1 illustrates the anticipated impact of background DOM on the breakthrough curve (as computed using MADAM) in a fixed-bed adsorber for a target organic compound as quantified by the alteration of relevant model input parameters. The organic compound in this exercise is assumed to have the characteristic adsorption isotherm and rate parameters given in Table 1 for a background of deionized distilled water

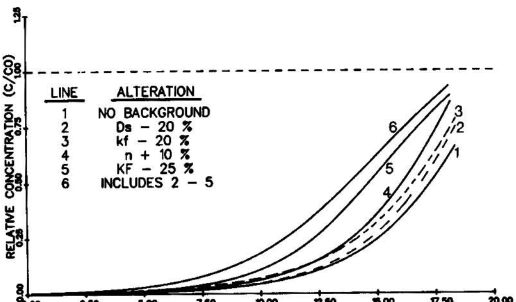


Figure 1. Predicted DBA breakthrough curves for lindane accounting for changes in adsorption parameters due to the presence of background components.

TABLE 1. ADSORPTION PARAMETERS FOR TARGET COMPOUND WITH NO BACKGROUND DOM

| Isotherm Parameters* | |
|---|---|
| Freundlich $K_F$ | 202 |
| Freundlich n | 0.48 |
| **Mass Transport Parameters** | |
| Film Diffusion, $k_f$ | $6.2 \times 10^{-3}$cm/s |
| Surface Diffusion, $D_s$ | $5.5 \times 10^{-12}$cm²/s |

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* Freundlich isotherm parameters are constants from the expression $q_e = k_f C_e^n$, with $C_e$ in mg/l and $q_e$ in mg/g.

As noted earlier, the presence of background DOM will often have an inhibitory effect on adsorption of target compounds, reflected in a decrease in both rate and capacity of removal. With this trend in view, lines 2 and 3 of Figure 1 are MADAM profiles for a 20 percent decrease in the surface diffusion and film diffusion coefficients, respectively, all other parameters remaining the same (line 1 is the case of no background DOM). As expected, these fluctuations in the rate coefficients imposed a shift in the breakthrough profile to the left, indicative of decreasing treatment effectiveness on the part of the carbon column.

The case of a 10-percent increase in the isotherm slope, n, is depicted as line 4 in Figure 1. Freundlich isotherm slopes for a given compound may not be appreciably altered by the presence of DOM, even in significant quantities [6]. Alterations in adsorption capacity prompted by the presence of background DOM appear most often as parallel displacements of the adsorption isotherm for pure solution. This shift is quantified in the Freundlich equation by changes in $K_F$. The MADAM profile for a 25 percent reduction in $K_F$ is shown as line 5. Profiles 4 and 5 indicate that the model for this particular system is more sensitive to the isotherm parameters than to the rate parameters, a trend observed in numerous carbon adsorption/modeling applications.

Profile 6 completes the family of curves as it includes all of the modified isotherm and mass transport parameters mentioned above. Several pertinent observations derive from the preceding exercise. First, when the presence of background DOM is found to alter the adsorption of target compounds from pure solution behavior, the new breakthrough profile can potentially be predicted using modified model input parameters, namely the isotherm and mass transport coefficients, which can be measured directly for the specific target compound in the presence of the designated background water. Second, a decrease of just 10 to 25 percent in the isotherm and/or rate parameters may constitute a significant decrease in a column's treatment efficiency for a target compound (where efficiency is defined as the volume of water that can be treated to a prescribed effluent level). Lastly, if a background water is found to alter the adsorption parameters and subsequently the breakthrough profile for the target compound, the magnitude of this impact will be a function of some quantified "strength" of the background water (e.g. measured as a surrogate parameter concentration such as TOC).

### Experimental Data

Bottle-point isotherm and SBA and DBA experiments were conducted for four different synthetic contaminated waters distinguished by the concentration of background humic acid in each. The four solutions contained a lindane concentration of 600 μg/l and alternate humic acid concentrations of 0, 2.5, 6.0, and 12.2 mg/l as TOC, respectively. While the above work was performed for a solution pH of 7, possible pH effects were examined by conducting an additional set of experiments for the 600 μg/l lindane — 6.0 mg/l humic acid solution at pH 4.

### Equilibrium Studies/Modeling

Adsorption equilibrium data for lindane in the presence of background humic acid at variable concentrations is shown in a log-log format in Figure 2. The adsorption capacity of lindane is indeed seen to decrease with increasing background concentration of the humic acid, due either to direct competition between the components for carbon sites or through solute-solute interactions which render the lindane molecules less hydrophobic. If the system is modeled in terms of lindane only with the humics treated as a system-specific background, a simple Freundlich model is adequate for describing the data. The Freundlich equation (referred to previously in Table 1) is a semi-empirical model of the form:

$$q_e = K_F C_e^{\,n} \tag{2}$$

where $q_e$ and $C_e$ are equilibrium solid and solution phase solute concentrations, respectively, and $K_F$ and n are characteristic isotherm parameters obtained from a logarithmic linearization of the data. Table 2 lists the Freundlich isotherm coefficients for this modeling approach. Background water impacts on adsorption capacity are reflected in changing values of the constant $K_F$ as the isotherm slopes remain essentially unchanged in every case. Parameter values for comparative tests at pH 4 are also included, and yield an interesting result. Whereas the isotherm capacity of lindane (as given by the $K_F$ value) differs by less than 7 percent for pH 7 and 4 in pure solution, the capacity is reduced by 25 percent for a pH change of 7 to 4 in a background of 6.0 mg/l as TOC of humic acid. Binary isotherm studies also revealed that humic acid adsorption is enhanced for reduced pH in the combined solution. This is consistent with single-solute isotherm studies for humic acid conducted in this work and results reported by other researchers [3]. Hence it appears that the humic molecules compete more favorably with lindane for available adsorption sites under more acidic conditions.

Table 3 lists isotherm model coefficients for an alternative modeling approach, namely the treatment of lindane and humic acid as independent compounds in a two-component system. The multisolute equilibrium equation applied in this analysis is a modified empirical Freundlich-Langmuir type competitive model after Fritz and Schluender [*18*].

$$q_{e,j} = \frac{A_j C_{ej}^{\,(B_j + B_{jj})}}{\mathrm{CONS}_j + \sum\limits_{j=1}^{N} A_{jk} C_{ek}^{\,B_{jk}}} \;;\; j = 1,2,\ldots,N \text{ and } A_{jk} = 1 \text{ when } j = k \tag{3}$$

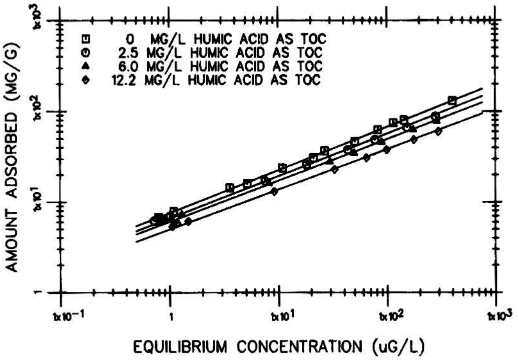

**Figure 2. Isotherms for lindane in humic acid at pH 7.**

TABLE 2. FREUNDLICH ISOTHERM PARAMETERS FOR LINDANE MODELED AS A SINGLE SOLUTE IN HUMIC ACID BACKGROUND WATER*

| Humic acid Concentration (mg/l as TOC) | pH | $K_F$ | n |
|---|---|---|---|
| 0.0 | 7 | 202 | 0.48 |
| 2.5 | 7 | 168 | 0.47 |
| 6.0 | 7 | 142 | 0.46 |
| 12.2 | 7 | 107 | 0.44 |
| 6.0 | 4 | 108 | 0.43 |

* Based on Equation 2 with $C_e$ in mg/l and $q_e$ in mg/g.

TABLE 3. BINARY SOLUTE ISOTHERM PARAMETERS*

| Parameters | pH = 7.0 | | | pH = 4.0 |
|---|---|---|---|---|
| | HA = 2.5 mg/l | HA = 6.0 mg/l | HA = 12.2 mg/l | HA = 6.0 mg/l |
| $A_1$ | 202 | 202 | 202 | 188 |
| $B_2$ | 0.48 | 0.48 | 0.48 | 0.44 |
| $B_{11}$ | $2.8\times10^{-5}$ | $4.7\times10^{-6}$ | $2.1\times10^{-6}$ | $3.1\times10^{-2}$ |
| $A_{12}$ | $1.4\times10^{-2}$ | $9.7\times10^{-3}$ | $2.3\times10^{-2}$ | $5.4\times10^{-1}$ |
| $B_{12}$ | 3.1 | 2.1 | 1.4 | 0.16 |
| $A_2$ | 3.8 | 2.4 | 0.84 | 3.8 |
| $B_2$ | 1.6 | 1.4 | 1.6 | 1.4 |
| $B_{22}$ | $1.8\times10^{-5}$ | $1.4\times10^{-5}$ | $6.7\times10^{-1}$ | $3.0\times10^{-4}$ |
| $A_{21}$ | 1.5 | $4.7\times10^{-1}$ | $9.3\times10^{-15}$ | $8.6\times10^{-1}$ |
| $B_{21}$ | $4.4\times10^{-2}$ | $3.3\times10^{-3}$ | $5.3\times10^{-4}$ | $1.9\times10^{-2}$ |

* Based on Equations 4 and 5 with $C_{e,j}$ in mg/l and $q_{e,j}$ in mg/g.

where $A_j$, $B_j$ CONS, $A_{jk}$ and $B_{jk}$ are isotherm constants. For the case of N = 2 (i.e. two-component system) and for single-solute equilibrium partitioning described by a Freundlich model (Equation 2), Equation 3 for components 1 and 2, respectively, simplifies to:

$$q_{e,1} = \frac{A_1 C_{e,1}^{\,(B_1 + B_{11})}}{C_{e,1}^{\,B_{11}} + A_{12}\, C_{e,2}^{\,B_{12}}} \tag{4}$$

$$q_{e,2} = \frac{A_2 C_{e,2}^{\,(B_2 + B_{22})}}{C_{e,2}^{\,B_{22}} + A_{21}\, C_{e,1}^{\,B_{21}}} \tag{5}$$

where $A_j$ and $B_j$ correspond to the Freundlich $K_F$ and n coefficients for component j. This expression provides excellent description of the bisolute equilibrium data. Correlation errors for data vs. model computations are less than 3 percent for lindane and less than 5 percent for humic acid. Most two-component systems utilizing this model result in a single set of constants to describe adsorption equilibria for varying concentrations of either solute. Single solute isotherms for humic acid, however differ for even small variations in initial concentration owing to the complex nature of humic substances. This phenomenon necessitates a separate model calibration for discriminate background concentrations of humic acid. Single-solute Freundlich isotherm coefficients for humic acid are given as $A_2$ and $B_2$ in Table 3.

### Fixed-Bed Adsorber Studies/Modeling

MADAM was used to compute the mass transport parameters for each lindane—humic acid combination by calibrating the model for SBA data. As stated previously, this involved simultaneous determination of the film and surface diffusion coefficients using two modeling approaches. First, lindane was singled out as a target compound with the humic acid considered simply as a part of the background water characteristics. Equilibrium and rate parameters were then evaluated in terms of lindane only, using the simple Freundlich isotherm equation in conjunction with a single-solute version of MADAM. In the second approach, humic acid was considered as an additional component and the analysis performed using the modified empirical competitive isotherm model (Equation 3) and a two-component version of MADAM. The adsorption parameters deriving from these two approaches for the SBA runs of the various systems studied are presented in Table 4.

As in the case of the isotherm parameters, the mass transport coefficients reflect an impact of the presence of DOM on the adsorption of lindane. Using either modeling approach, the rates of film and intraparticle mass transport decrease in the presence of humic acid, and this trend is proportional to the humic acid concentration for a given initial concentration of lindane. Thus both the capacity and rate of adsorption of lindane are reduced by the presence of background DOM and, as suggested in the hypothetical exercise summarized by Figure 1, this combined impact can potentially translate into a significant decline in adsorber performance with respect to the target compound. The practical implications of this impact for the specific system under study are illustrated in Figure 3, which shows MADAM DBA profiles for lindane for varying concentrations of humic acid.

The primary mechanism accounting for the reduction in lindane adsorption is not readily apparent. The decrease in intraparticle mass transport may be due in part to the large molecular structure of humic acids acting to retard migration of lindane molecules within the micropores of carbon particles. Aquatic humics have also demonstrated a tendency to form complexes with organic micropollutants [*19*, *20*]. It is conceivable, therefore, that a portion of the lindane molecules associate with humic acids in binary solutions. This activity may contribute to the lower film diffusion transport for lindane, since binary system values for the humic acid are an order of magnitude less at pH 7. The opposite trend exists in the case of intraparticle transfer, however, in that surface diffusion coefficients for lindane decrease in the presence of the background water even though values for the humic acid are appreciably higher. It is interesting to note in this context that both film and surface diffusion of humic acid increase with increasing humic concentration. This is likely attributable to the enhanced driving force of the humics in solution, but whether or not this increasing concentration gradient also augments complexation with lindane cannot be determined without further study.

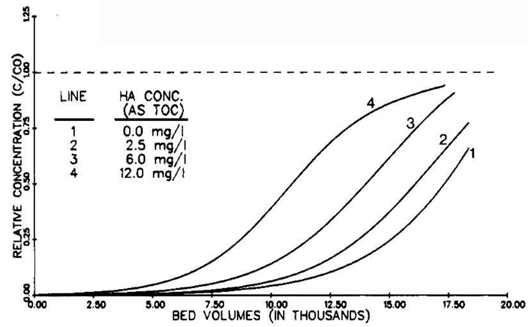

**Figure 3. Predicted DBA breakthrough profiles for lindane in the presence of varying background concentrations of humic acid.**

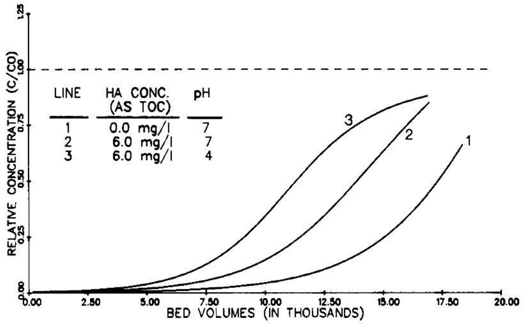

**Figure 4. Predicted DBA breakthrough profiles for lindane in the presence of varying background concentrations of humic acid at pH 4 and 7.**

Adsorption data at pH 4 may shed additional light on removal mechanisms and related phenomenological effects. Figure 4 presents MADAM DBA profiles for lindane using the single-solute modeling approach for two background concentrations of humic acid and two pH values. The column results follow the equilibrium studies in terms of illustrating a significant decrease in lindane removal for a pH drop from 7 to 4 when background DOM is present. Both modeling approaches yield lower film and surface diffusion coefficients for the target compound at the lower pH value. This trend would appear to counter the notion of lindane—humic acid association being the predominant mechanism responsible for reduced rate and capacity of lindane adsorption, inasmuch as humic acid rate and capacity are increased over this pH change. Rather, the result suggests that direct competition between the two adsorbing solutes is the primary solute-solute interaction. Final judgement on the issue requires further study, however, because the magni-

TABLE 4. SBA MADAM CALIBRATION PARAMETERS

| | | | | Bisolute Calculations | | | Lindane as Single Solute | | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | $C_0$* (mg/l) | pH | $v_z$ (cm/s) | $D_g$** ($x10^{-3}$) | $k_f$ ($cm/sx10^3$) | $D_s$ ($cm^2/sx10^{12}$) | $D_g$** ($x10^{-3}$) | $k_f$ ($cm/sx10^3$) | $D_s$ ($cm^2/sx10^{12}$) |
| Lindane | 0.6 | 7 | 0.55 | 148.8 | 6.2 | 5.5 | 148.8 | 6.2 | 5.5 |
| Lindane | 0.6 | 7 | 0.56 | 24.4 | 5.8 | 2.0 | 124.0 | 6.2 | 5.0 |
| Humic Acid | 2.5 | | | | 0.3 | 7.0 | | | |
| Lindane | 0.6 | 7 | 0.55 | 11.2 | 4.7 | 1.5 | 105.8 | 5.3 | 4.6 |
| Humic Acid | 6.0 | | | | 0.3 | 7.2 | | | |
| Lindane | 0.6 | 7 | 0.54 | 5.6 | 4.3 | 0.6 | 80.3 | 4.5 | 4.3 |
| Humic Acid | 12.2 | | | | 0.4 | 8.9 | | | |
| Lindane | 0.6 | 4 | 0.55 | 9.5 | 4.3 | 0.5 | 81.3 | 4.8 | 4.3 |
| Humic Acid | 6.0 | | | | 1.1 | 8.6 | | | |

* Humic acid concentrations are in mg/l as TOC
** Dg—Solute distribution parameter (dimensionless)

tude and rate of association is likely dependent upon variations in pH.

One peculiarity is evident in the surface diffusion coefficient values computed for lindane by the bisolute modeling approach. While the values for $D_s$ appear to descend in a consistent pattern for varying humic acid concentrations in the single-solute approach, there is a substantial "jump" from $5.5 \times 10^{-12}$cm²/s for no background to $2.0 \times 10^{-12}$cm²/s for a background humic concentration of just 2.5 mg/l as TOC using the bisolute model. This anomaly can be explained in terms of the dimensionless solute distribution parameter, $D_g$, also listed in Table 4 for each calibration. The MADAM algorithm utilizes $D_g$ in the expression that de-dimensionalizes a term which includes $D_s$ for solution of the solid phase material balance equation. Thus abrupt changes in $D_g$ may result in a similar discontinuity of the same direction in $D_s$ for variable calibration runs. The solute distribution parameter is given by:

$$D_g = \rho(1-\epsilon)\sum_{i=1}^{N} q_{o,i} \Big/ \left(\epsilon\sum_{i=1}^{N} C_{o,i}\right) \qquad (6)$$

which for a single solute system is:

$$D_g = \frac{\rho\,(1-\epsilon)\,q_o}{C_o\epsilon} \qquad (7)$$

and for a two-component case:

$$D_g = \frac{\rho(1-\epsilon)\ (q_{o,1} + q_{o,2})}{\epsilon(C_{o,1} + C_{o,2})} \qquad (8)$$

where $\rho$ is carbon particle density ($M/L^3$), $\epsilon$ is bed void ratio (dimensionless), and $q_{o,i}$ is the solid phase concentration of species i corresponding to the initial liquid phase solute concentration, $C_{o,i}$, as given by the appropriate solute equilibrium partitioning expression. The point of issue arises in this particular two-component case owing to the large disparity in conditions and equilibrium partitioning between lindane and humic acid. For lindane with no background DOM, $D_g$ is given simply by Equation 7. However, for the cases containing background humic acid, the $q_o$ term is expanded to include a term for humic acid, and similarly for $C_o$ in the denominator. The $q_o$ term is increased, but only slightly, because the adsorption capacity of lindane on F-400 is much greater than that of the humic acid for the concentration ranges chosen in this work. Conversely, the $C_o$ values for humic acid are large compared to those for lindane, resulting in a fivefold increase in the denominator for Equation 8 for even the most conservative case; i.e., a humic acid background concentration of 2.5 mg/l. This variation accounts for the $D_g$ values from bisolute modeling being an order of magnitude less than those computed in the single-solute methodology, and the subsequent unexpected shift in $D_s$ values determined by MADAM.

Figures 5 through 10 show column data and model profiles for selected SBA/DBA pairs, and demonstrate the utility of MADAM for predicting DBA performance via the two modeling approaches investigated. All six figures are for the case of 6.0 mg/l TOC humic background. Figures 5 and 6 illustrate the single-solute modeling approach at pH 7; Figures 7 and 8 show the bisolute analysis of the same system; and Figures 9 and 10 depict single-solute modeling of lindane at pH 4. Deviations between experimental and predicted profiles for lindane are slightly larger for most cases for the bisolute modeling approach, but the differences are insignificant. The bisolute model was also able to adequately predict breakthrough of humic acid in most cases. A distinct advantage of the single-solute approach is the reduced input requirements and computational effort compared to multicomponent modeling. In addition, more difficulties are encountered with respect to numerical stability in the bisolute MADAM computations, especially in a system such as the one studied where the two species have such diverse

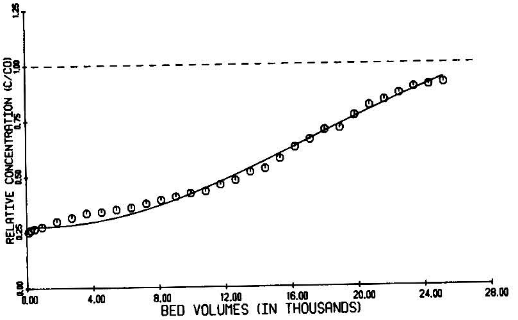

Figure 5. SBA data and model calibration for lindane in humic acid background of 6.0 mg/l as TOC.

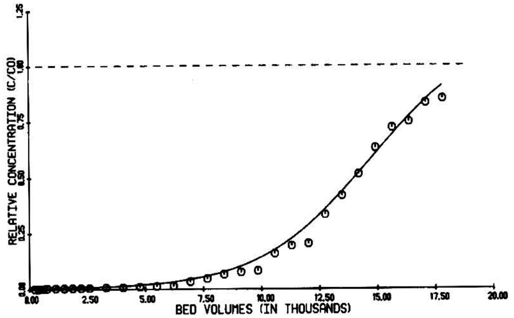

Figure 6. DBA data and predicted profile for lindane in humic acid background of 6.0 mg/l as TOC.

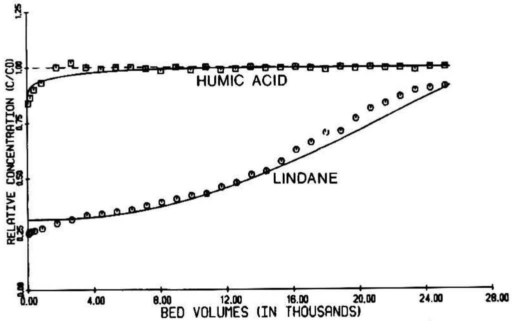

Figure 7. SBA data and calibration profiles for lindane and humic acid ($C_o$ = 6.1 mg/l as TOC).

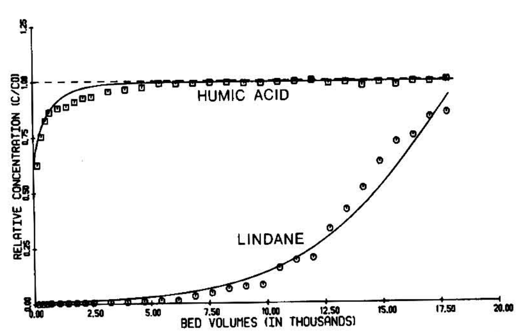

Figure 8. DBA data and predicted profiles for lindane and humic acid ($C_o$ = 6.0 mg/l as TOC).

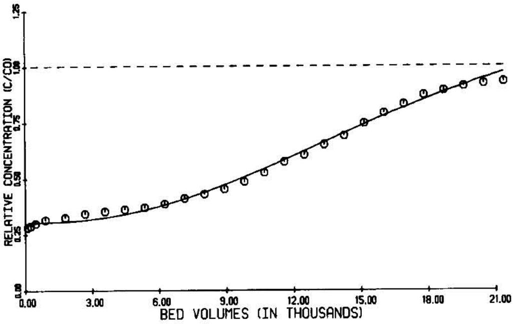

Figure 9. SBA data and model calibration for lindane in humic acid background of 6.0 mg/l as TOC at pH 4.

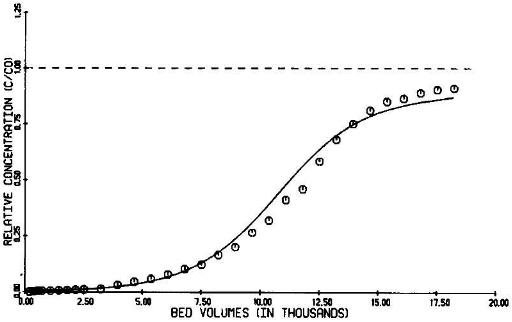

Figure 10. DBA data and predicted profile for lindane in humic acid background of 6.0 mg/l as TOC at pH 4.

adsorptive properties (at least with regards to adsorption capacity). The bisolute approach, however, does offer the advantage in this case of predicting the breakthrough of the background component, knowledge of which may be important in certain applications.

## CONCLUSIONS

GAC adsorption of a target organic compound in the presence of background DOM (in the form of a commercial humic acid) was analyzed by two modeling approaches using a mathematical adsorption model, MADAM. The major findings and conclusions of the study are summarized below.

1. The capacity and rate of lindane adsorption were found to decrease in the presence of background humic acid. This decrease was proportional to the concentration of humic acid in solution as given by a lumped parameter, TOC. The reduced removal of the target compound was reflected in both isotherm and rate coefficients determined experimentally. In contrast, rate coefficients for humic acid increased for increasing humic concentration in the binary system. Direct competition and solute-solute interactions which render lindane molecules less hydrophobic appear to be important mechanisms operative in the system studied.

2. When humic acid was present, the capacity and rate of lindane adsorption was significantly reduced for a pH drop from 7 to 4. This coincided with a sizeable increase in the adsorption parameters measured for the background organic matter.

3. The SBA technique was verified as a useful tool for determination of kinetic parameters for the system studied. When applied in conjunction with CMBR isotherm parameters, MADAM calibrations of SBA breakthrough data yielded film and surface diffusion coefficients which enabled adequate predictions of DBA breakthrough profiles for lindane in the presence of varying concentrations of humic acid.

4. A bisolute version of MADAM sufficiently calibrated and predicted fixed-bed adsorber profiles for lindane and humic acid where the system is treated as a binary solution. A second modeling approach was investigated in which adsorption equilibrium and rate parameters were experimentally determined and modeling performed for a designated target compound (in this case, lindane) in the presence of a theoretically unspecified background water. A single-solute version of MADAM again successfully calibrated and predicted fixed-bed adsorber results. Due to its reduced input and computational requirements and ease of implementation, this latter approach may prove a very practical modeling methodology for applications where the primary concern is removal of one or a few known target organic compounds, especially in consideration of the difficulty in accurately characterizing the complex background waters in which they are often present.

## ACKNOWLEDGMENT

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## NOMENCLATURE

$A_j$ = Freundlich equilibrium capacity constant in bisolute isotherm model
$A_{jk}$ = Bisolute isotherm constant
$B_j$ = Freundlich equilibrium energy constant in bisolute isotherm model
$B_{jk}$ = Bisolute isotherm constant
$C_e$ = Equilibrium liquid phase solute concentration (mg/l)
$C_0$ = Initial liquid phase solute concentration (mg/l)
$D_g$ = Solute distribution parameter (dimensionless)
$D_s$ = Intraparticle surface diffusion coefficient (cm$^2$/s)
$K_F$ = Freundlich equilibrium capacity constant
$k_f$ = Film transfer coefficient (cm/s)
M = Carbon dose (g adsorbent/l solution)
n = Freundlich equilibrium energy constant
$q_0$ = Equilibrium solid phase solute concentration corresponding to $C_0$ (mg solute/g adsorbent)
$q_e$ = Equilibrium solid phase solute concentration corresponding to $C_e$ (mg solute/g adsorbent)
$v_z$ = Interstitial flux velocity (cm/s)
$\epsilon$ = Adsorbent bed void fraction (porosity)
$\rho$ = Adsorbent density (g/cm$^3$)

## ADDENDUM

A related paper published previously in *Environmental Progress*, (4, 105-111, May 1985) and cited here as reference 10 contains the following errata.

1. The labels "Least Diverse" and "Most Diverse" in the legend in Figure 1 should be interchanged.

2. "Sc", not "Sh", should appear in Equation 2. The following line should read: "Sc is the dimensionless Schmidt number" instead of "Sh is the dimensionless Sherwood number."

3. The next sentence should read: "Film transfer coefficients . . . ranged from $3.1 \times 10^{-3}$ to $3.6 \times 10^{-3}$ cm/s" instead of "Film transfer coefficients . . . ranged from $4.3 \times 10^{-3}$ to $5.3 \times 10^{-3}$ cm/s. Thus, in the following sentence, "110%" should be "45%".

4. The Sherwood Number values given in Table 6 should read (from top to bottom) as: "35, 23, 31, 19, 32".

5. The values of DBA standard deviation in Table 8, i.e. 3.8 and 12.6, should be interchanged.

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# Evaluation of Sorbents and Additives for Dry $SO_2$ Removal

**Claus Jorgensen and John C. S. Chang**

Acurex Corporation, Southeast Regional Office, P.O. Box 13109,
Research Triangle Park, NC 27709

and

**Theodore G. Brna**

U.S. Environmental Protection Agency, Air and Energy Engineering Research Laboratory,
Research Triangle Park, NC 27711

*Bench scale studies of the reaction between sulfur dioxide and alkaline sorbents were performed in an integrated fixed bed reactor at low temperature, simulating the fabric filter dust layer of dry FGD systems with* $SO_2$ *laden gas passing through it. Three major groups of sorbents were tested: calcitic and dolomitic hydrated lime, sodium bicarbonate, and limestone (calcite and aragonite) with salt additives such as* $CaCl_2$, $Ca(NO_3)_2$, *and* $NaNO_3$. *Relative humidity significantly affected* $SO_2$ *absorption by lime and limestone plus additives, but had less impact on* $NaHCO_3$ *reactivity. Different reaction patterns for various sorbents were observed: the* $SO_2$/*hydrated lime reaction rate was reduced with conversion of the sorbent, resulting in limited lime utilization, whereas the reactions between* $SO_2$ *and* $NaHCO_3$ *and* $SO_2$ *and* $CaCO_3$ *plus additives seem to proceed a constant rate, potentially leading to high sorbent utilizations. Results are discussed relating to sorbent screening for dry FGD systems.*

## INTRODUCTION

The increased interest in dry flue gas desulfurization (FGD) processes for removal of sulfur dioxide ($SO_2$) over the last 5-10 years (specifically, the perceived need for testing, evaluating, and comparing various sorbents) has spurred the development of bench-scale apparatus to study specific FGD reactions prior to actual pilot-scale testing [*1*-*7*]. Some researchers used a differential reactor for studying the reaction kinetics; others used an integral sand bed reactor for measuring the initial rate of reaction of $SO_2$ with sorbent. The present work also uses a sand bed reactor for studying the reaction of gaseous $SO_2$ with solid sorbent, similar to an alkaline dust cake on a fabric filter with $SO_2$-laden flue gas passing through it. Changes in gas phase and sorbent composition during the reaction are included in the present study as they are believed to play a significant role for any industrial application.

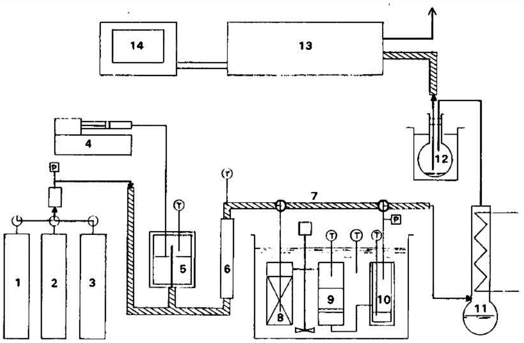
Sorbents investigated in this work included hydrated limes, sodium bicarbonate, and limestone. Various sorbent qualities, particle sizes, and sorbent additives were tested. While performance comparisons between the various sorbents are emphasized, some reaction rate controlling models for relating performance differences between the various sorbents are also proposed and discussed.

## EXPERIMENTAL APPARATUS AND TESTING FEATURES

The experimental apparatus shown in Figure 1 was developed using recommendations from other research groups performing similar studies (e.g., Gary T. Rochelle's group at the University of Texas [*6*, *7*]) and from experience gained in initial tests stressing data quality and data repeatability. The core of the experimental apparatus is the sand bed reactor where the $SO_2$ in the test gas reacts with the alkaline sorbent. The sand bed reactor is a vertical packed bed of approximately 1 g sorbent dispersed in (normally) 40 g inert silica sand; the entire bed is supported on a 4.5 cm diameter fritted glass plate contained in a glass cylinder. The simulated flue gas passes down through the sand bed at a face velocity of up to 6 cm/s.

The three process variables expected to influence the $SO_2$ capture by the sorbent are: the $SO_2$ concentration in the simulated flue gas, the dry bulb temperature of the gas, and the relative humidity.

In the present work, it was decided to use pure nitrogen for simulating the dry flue gas composition. Data from Rochelle indicated no effects of oxygen and carbon dioxide on $SO_2$ absorption in the sand bed reactor. While separate injection of $SO_2$ gas into the nitrogen gas stream is possible, the need for very accurate control of small gas



1. N2 supply
2. Span gas
3. Test gas
4. Syringe pump
5. Evaporation chamber
6. Electrical heater
7. By-pass line
8. Back-mix chamber
9. Sand bed reactor
10. Wet bulb thermometer
11. Condenser
12. Water trap (ice)
13. SO2 analyzer
14. Recorder

**Figure 1. Experimental apparatus.**

flows dictated the use of commercially available calibrated span gases of $SO_2$ in nitrogen ($SO_2$ concentration range of 500-2000 ppm) as the test gas.

The desired temperature range of 54-85°C (130-185°F) was obtained by heating the test gas prior to its entering the reactor and immersing the entire reactor vessel in a thermostated water bath.

Since a broad range of moisture content in the flue gas was needed for testing, water was continuously and accurately injected using a syringe type dispensing pump, equipped with two syringes to allow continuous operation with transient-free switchover periods. Steady evaporation was achieved using a separate hot evaporation chamber (sand reservoir heated to 150-200°C (approximately 300-400°F)) prior to mixing the vapor with the test gas. A "back-mix chamber" in the water-bath-heated section of the apparatus ensured uniformity of the gas mixture entering the sand bed reactor.

The dry bulb temperature was measured just above the sand bed reactor. The exact wet bulb temperature was measured just downstream of the reactor using a wetted wick thermometer. The difference between dry and wet bulb temperatures is the "approach to saturation," $\Delta t_s$, which together with the pressure measurement (U-tube manometer) establishes the relative humidity at test conditions. Measurement of the water injection, water collection, and gas flow rates permitted calculation of gas humidity and served as a quality control check on this important test parameter.

Prior to testing, the sand bed reactor was by-passed, and the test gas $SO_2$ concentration was established with a DuPont 411 $SO_2$ analyzer by comparison with a standard of higher $SO_2$ concentration (normally up to 3000 ppm). The water injection/condensation system was normally operated during the $SO_2$ calibration procedure. Water/$SO_2$ equilibrium data [8] suggest that any $SO_2$ capture by the condensed water would amount to less than 2-3 percent of the total amount of $SO_2$ in the gas phase. This was confirmed by repeated comparisons of $SO_2$ analyzer data using dry gas calibration followed by calibration with water injection/condensation operation. During testing, the gas passed from the sand bed reactor via the water condensation system to the $SO_2$ monitor, and $SO_2$ absorption in the sand bed reactor was established by integration of the recorded $SO_2$ concentration/time curve.

## SAND BED REACTOR MODEL

Work by others [5] suggests that satisfactory dispersion of sorbent in the sand bed (i.e., good mixing and little agglomeration of sorbent particles) seems to be achieved when using 40 g sand per 1-2 g sorbent. The satisfactory repeatability of results obtained in the present work seems to support this assumption. The sand bed containing the alkaline sorbent is of cylindrical shape (approximately 4.5 cm in diameter and 1.6 cm in length when using 40 g sand). Supplier specification of the sand (Ottawa Industrial Sand Co., Grade F-70) and independent measurements indicate a bed voidage of $\epsilon = 0.40$. The intensity of dispersion can be estimated using the methods of Levenspiel [9] for calculation of the Reynolds, Re, and Schmidt, Sc, numbers normally used in the tests:

$$\mathrm{Re} = \frac{d_p u \rho}{\mu}$$

$$= \frac{(1.4 \times 10^{-2}) \times (6.0) \times (1.0 \times 10^{-3})}{190 \times 10^{-3}} \simeq 0.4 \qquad (1)$$

$$\mathrm{Sc} = \frac{\mu}{\rho D_{SO_2}}$$

$$= \frac{190 \times 10^{-3}}{(1.0 \times 10^{-3}) \times (0.156)} \simeq 1.2 \qquad (2)$$

where $d_p$ = particle diameter, cm   $\rho$ = gas density, g/cm³
$u$ = face velocity, cm/s   $\mu$ = gas viscosity, g/cm-s
$D_{SO_2}$ = $SO_2$ molecular diffusion coefficient, cm²/s

Using the chart in Reference 9 for a plug-flow fixed-bed reactor with $\epsilon = 0.40$ gives a dispersion coefficient, D, of 0.132. From the above data for the sand bed, the dispersion number becomes:

$$\frac{D}{uL} = \frac{0.132}{(6.0) \times (1.6)} = 0.014 \qquad (3)$$

where L is the height of sand bed reactor in centimeters.

This low dispersion number suggests that the effects of mixed flow probably can be disregarded and that a plug flow model is a reasonable assumption.

The accepted model for this type of heterogeneous reaction is the unreacted core model in which the reaction starts at the outer skin of the particle, and the zone of reaction then moves progressively into the particle, leaving behind completely converted reaction products, or ash. Applying this model for the $SO_2$/sorbent reaction, the following three reaction steps are proposed, each of which potentially could control the overall rate of conversion of $SO_2$ with sorbent:

1. Diffusion of gaseous $SO_2$ to the surface of the solid particle.
2. Penetration and diffusion of $SO_2$ through the ash layer to the surface of the unreacted core.
3. Reaction of $SO_2$ with sorbent at the core reaction surface.

While the present test work does not aim to completely establish the system's reactions for different sorbents using any of the above mechanisms with related rate constants, such a model can be very helpful in interpreting and evaluating data. The difficulty in precisely determining any of the above mechanisms as the sole overall rate controlling step using data from the sand bed reactor is related to the semi-batch characteristics of the experimental apparatus (the $SO_2$ flow is continuous over a batch of sorbent), which increases the probability of having different mechanisms controlling the overall rate at different times.

Relative to the gas film diffusion step, the dispersion of the solid sorbent in an inert silica sand avoids both channeling and by-passing of the sorbent, enabling a uniform gas flow with well defined gas/solid contact. Assuming satisfactory dispersion of sorbent without significant agglomeration, the mass transfer number for $SO_2$ from the gas phase to sorbent surface can be estimated using the modified Reynolds number [8]:

$$\overline{\mathrm{Re}} = \frac{d_p \mu \rho}{\mu (1 - \epsilon)}$$

$$= \frac{(1.4 \times 10^{-2}) \times (6.0) \times (1.0 \times 10^{-3})}{(190 \times 10^{-3}) \times (0.60)} = 0.74 \qquad (4)$$

Colburn's j-factor for mass transfer [8] is:

$$j_D = 5.7 \times (\overline{Re})^{-0.78} = 5.7 \times (0.74)^{-0.78} = 7.2 \qquad (5)$$

Using the earlier calculated Schmidt number, the gas transfer number is:

$$k_g = j_D \frac{G}{M} Sc^{-2/3} = (7.2) \frac{(0.0057)}{(28)} (1.2)^{-2/3}$$

$$= 1.3 \times 10^{-3} \text{ mol/cm}^2\text{-s} \qquad (6)$$

where $G$ = mass gas flow, g/cm$^2$-s
$M$ = gas molecular weight, g/mol

A gas transfer coefficient of $1.3 \times 10^{-3}$ mol/cm$^2$-s suggests a very fast mass transfer rate from gas to solid sorbent. Using the equation from Levenspiel (9) expressing time, $\tau$, for complete reaction of a solid particle with a gas and assuming that gas film diffusion is rate controlling:

$$\tau = \frac{\rho_\beta R}{3 b k_g C_{Ag}}$$

$$\simeq \frac{(0.03) \times (5 \times 10^{-4})}{3 \times 1 \times (1.3 \times 10^{-3}) \times (5 \times 10^{-4})} = 7.7 \text{ sec} \qquad (7)$$

where $\rho_\beta$ = sorbent particle molar density, for calcium hydroxide [$Ca(OH)_2$], mol/cm$^3$
$R$ = sorbent particle radius, cm
$b$ = reaction stoichiometry for $Ca(OH)_2$
$C_{Ag}$ = bulk concentration of $SO_2$ in gas phase (for 500 ppm), mol $SO_2$/mol gas

This example suggests that a 10 μm diameter hydrated lime particle would react totally with $SO_2$ in a matter of seconds if gas-phase diffusion were the overall rate controlling step. As the measured time for reaction is much longer (as will be seen, significant amounts of unconverted sorbent are found even after 1 hr reaction), gas film diffusion can probably be excluded as the overall rate controlling step. This result also indicates that the actual gas face velocity chosen would not impact the overall rate of reaction.

## EXPERIMENTS AND RESULTS

### Results Using Hydrated Limes as Sorbents

As the present test work compares performance between various sorbents and the effect of changing selected process conditions, a "baseline" sorbent and some standard operating conditions were chosen: 1 g of reagent grade $Ca(OH)_2$ (Fisher C-97) dispersed in 40 g sand, the sand bed reactor operated at 64.4°C (148°F), and 325 l/h (approximately 10 scfh) nitrogen with 500 ppm $SO_2$ supplied to the reactor. A reference time of one hour was used for testing.

A typical $SO_2$ outlet concentration/time curve for a single run is shown in Figure 2. Zero outlet concentration was measured during the initial testing period, but later the $SO_2$ outlet concentration rises and approaches that of the inlet, indicating no further $SO_2$ absorption taking place in the reactor. The total amount of $SO_2$ absorbed during the run was found by integration of the area above the recorded curve, and comparison of the $SO_2$ absorbed with the amount of $Ca(OH)_2$ initially present led to the conclusion that a significant amount of $Ca(OH)_2$ (60-90 percent) had not reacted with $SO_2$. This result might be explained in terms of conventional theory as follows. Initially, no ash diffusion resistance exists, and all $SO_2$ reacts with fresh surface $Ca(OH)_2$. Ash building up on the particle surface causes the reaction rate to decrease and the sand bed outlet $SO_2$ concentration to rise. Eventually the reaction ceases, and the $SO_2$ outlet concentration equals the inlet concentration, which corresponds to the ash diffusion resistance having reached an extremely high value. "Blinding" of the sorbent surface is probably a better description of this phenomenon.

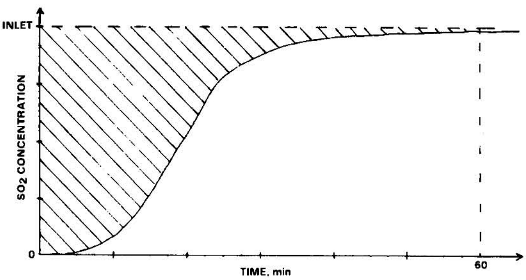


Figure 2. Generic strip chart from $SO_2$ analyzer using $Ca(OH)_2$ as sorbent in the sand bed.

Figure 3 depicts the amount of sorbent converted with $SO_2$ (mol $SO_2$/mol $Ca(OH)_2$ present) after one hour for different relative humidities. Although no definite proof can be given at this point, it seems that the ash diffusion resistance, being the most probable mechanism stopping the reaction ("blinding"), is strongly related to relative humidity in the gas phase, probably via water adsorption on the particle. An important implication of this "blinding" of the sorbent surface is that the total conversion cannot be in-

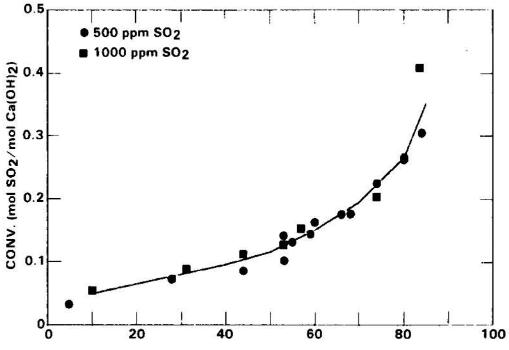


Figure 3. Conversion of reagent grade $Ca(OH)_2$ with $SO_2$ (1 hour) 1 g $Ca(OH)_2$, 64.4°C (148°F).

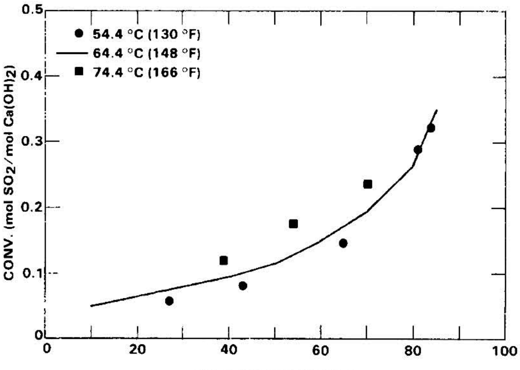


Figure 4. Conversion of reagent grade $Ca(OH)_2$ with $SO_2$ (1 hour) 1 g $Ca(OH)_2$, 500 ppm $SO_2$.

creased by increasing the $SO_2$ partial pressure in the gas phase. This was confirmed by tests using 1000 ppm $SO_2$ as shown in Figure 3.

Figure 4 shows the effect of temperature on $SO_2$ absorption. It appears that the conversion of $Ca(OH)_2$ with $SO_2$ increases somewhat with temperature for constant relative humidity, the order of magnitude is 20-30 percent per 10°C (18°F).

Some commercially available pressure hydrated limes have also been tested in the sand bed reactor. The results, shown in Figure 5, revealed somewhat lower $SO_2$ absorption by these hydrates in the range from 50 percent relative humidity, $\Delta t_s$ = 13°C (24°F), to 70 percent relative humidity, $\Delta t_s$= 7°C (12°F), than by reagent grade $Ca(OH)_2$. Using the BET surface area to compare results achieved in the sand bed reactor, a correlation between surface area and $SO_2$ absorption can be seen for the dolomitic samples, but none is apparent for the few calcitic types, based on these data.

Some inorganic salts were also tested as additives to reagent grade $Ca(OH)_2$: calcium chloride ($CaCl_2$), sodium chloride (NaCl), sodium hydroxide (NaOH), and sodium nitrate ($NaNO_3$). The results of these tests are depicted in Figure 6. Each was mixed with $Ca(OH)_2$ in a dry procedure, and not by the procedure of water dissolution and mixing with sorbent followed by drying, as done by others [*6, 7*]. The outlet $SO_2$ concentration/time curves were similar to those described above for pure $Ca(OH)_2$, but all additives shifted the ultimate $SO_2$ absorption somewhat. Continuing what was said earlier, this would indicate that the additive changes the ultimately controlling $SO_2$ ash "blinding" effect correspondingly. The most notable result is probably the quite significant increase in $SO_2$ absorption using $CaCl_2$ as additive. Relating to an earlier statement regarding water adsorption on the lime particles, it is believed that the $CaCl_2$, having a high water affinity ("hygroscopic salt"), increases the water absorbed by the particle, thereby reducing the $SO_2$ ash "blinding" effect.

### Results Using Sodium Compounds as Sorbents

Most bench-scale studies using sodium compounds as dry sorbents for $SO_2$ removal have been performed at temperatures in the range 150-250°C (300-500°F) [*1*]. Sodium bicarbonate, $NaHCO_3$, which has been extensively studied, thermally decomposes to anhydrous soda ash at these temperatures, which has often been claimed to be an important factor in the $SO_2$ removal process. The present work, however, focuses on the reactions at a lower temperature, 64.4°C (148°F), where the effect of thermal decomposition of $NaHCO_3$ is expected to be less significant. To investigate thermal decomposition effects, some comparison tests were done using different time periods for "conditioning" sorbent samples (at test conditions of temperature and humidity) prior to exposure to the $SO_2$ test gas. Subsequent testing, however, gave the same $SO_2$ absorption results, independent of differences in time periods of "conditioning."

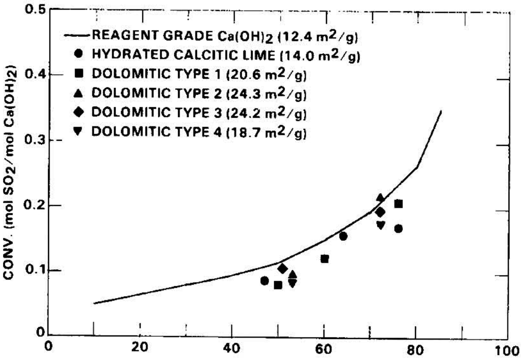


**Figure 5. Conversion of different hydrated limes with $SO_2$ (1 hour) 1 g sorbent, 64.4°C (148°F), 500 ppm $SO_2$.**

A typical $SO_2$ concentration/time curve as recorded by the $SO_2$ monitor using reagent grade (Fisher S-233) $NaHCO_3$ as sorbent in the sand bed reactor is shown in Figure 7. It appears that a steady $SO_2$ removal rate is established within a few minutes of sorbent exposure to $SO_2$. This nearly constant rate, or constant $SO_2$ removal efficiency, is maintained throughout the testing period, being reduced only slightly with the gradual consumption of sorbent. This is entirely different from what was observed above using $Ca(OH)_2$ as sorbent (Figure 2).

A series of tests at different relative humidities showed somewhat increased $SO_2$ absorption with increased humidity. Also, tests were made using different amounts of $NaHCO_3$ in the sand bed and different $SO_2$ concentration levels. To help interpret these results, a plug flow reactor model was adopted for which the performance equation is [9]:

$$\tau = C_{SO_2}{}^{\circ} \int_0^{X_{SO_2}f} \frac{dX_{SO_2}}{-r_{SO_2}} \qquad (8)$$

where $\tau$ = space time = $\frac{V\epsilon}{v_0}$, h

$V$ = sand bed volume, ml

$\epsilon$ = sand bed voidage, fraction

$v_0$ = gas volumetric flow, ml/h

$-r_{SO_2}$ = rate of disappearance of $SO_2 = \frac{-dC_{SO_2}}{dt}$, mol/l-h

$C_{SO_2}{}^{\circ}$ = inlet $SO_2$ concentration, mol/l

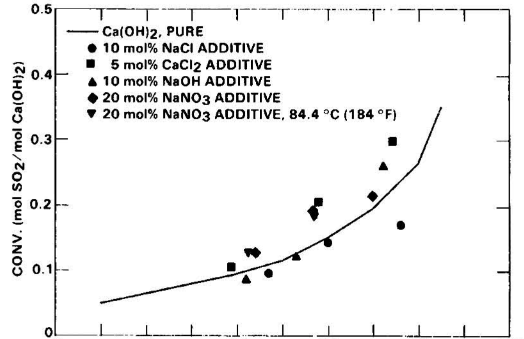


**Figure 6. Conversion of $Ca(OH)_2$ + additives with $SO_2$ (1 hour) 1 g $Ca(OH)_2$, 64.4°C (148°F), 500 ppm $SO_2$.**

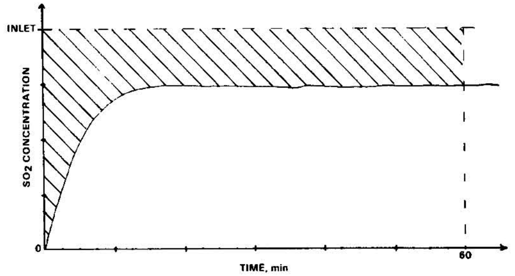


**Figure 7. Generic strip chart from $SO_2$ analyzer using $NaHCO_3$ (or $CaCO_3$ + additive) as sorbent in the sand bed.**

$X_{SO_2}$ = conversion of $SO_2$, fraction
$X_{SO_2f}$ = outlet conversion of $SO_2$, fraction

If the reaction rate is expressed as a first order reaction in both sorbent and $SO_2$, then:

$$-r_{SO_2} = kC_{sorb}C_{SO_2} = k\frac{N_{sorb}}{V(1-\epsilon)}C_{SO_2}^{\circ}(1 - X_{SO_2}) \quad (9)$$

where k = a rate constant for the reaction, l/mol-h
$C_{sorb}$ = concentration of sorbent in the sand bed, mol/l
$N_{sorb}$ = amount of sorbent in the sand bed, mmol

As the total amount of sorbent is fairly large, compared to the amount reacted during the reaction period of interest, assume:

$$N_{sorb} = N_{sorb}^{\circ} \text{ (initial amount of sorbent)}$$

Inserting these expressions in the performance equation (Equation 8) and expressing the sorbent as sodium oxide, $Na_2O$, yields:

$$\tau = \frac{V\epsilon}{v_0} = \frac{V(1-\epsilon)}{kN_{Na_2O}^{\circ}}\int_0^{X_{SO_2f}}\frac{dX_{SO_2}}{1-X_{SO_2}}$$

$$= \frac{V(1-\epsilon)}{k\,N_{Na_2O}^{\circ}}\left(-\ln\left(1-X_{SO_2f}\right)\right) \quad (10)$$

Rearranging,

$$-\ln\left(1-X_{SO_2f}\right) = k\frac{\epsilon}{v_0(1-\epsilon)}N_{Na_2O}^{\circ} \quad (11)$$

The left side of Equation 11 has been plotted versus $N_{Na_2O}^{\circ}$ for all test runs using $NaHCO_3$ as the sorbent and is depicted in Figure 8. In the low humidity range, the slopes of the linear curves indicate the rate constant, k, of 8, 18, and 25 × $10^3$ l/mol-h almost proportional to the corresponding relative humidities of 15, 30-35, and 45-50 percent, respectively. For higher relative humidity, 70-75 percent, interpretation of the results seems more complex in terms of the above equation; the plot reveals the same straight line slope as was observed at 50 percent relative humidity. Even at the quite high $SO_2$ absorption rates (at high humidity, the measured range covers 40-75 percent steady state $SO_2$ removal across the sand bed reactor), however, no reaction inhibiting effects such as "blinding" were seen. A probable mechanism could be the $CO_2$ released during reaction with $SO_2$ creating sufficient fresh surface of sorbent to account for the continued reaction.

A few test runs were also made using reagent grade anhydrous sodium carbonate, $Na_2CO_3$, (Fisher S-263) as sorbent. However, very low $SO_2$ absorption (less than 5 percent of that seen when using $NaHCO_3$), even at high relative humidity, was observed in the sand bed reactor, and no steady removal rate could be detected. Based on these data, it seems that the above reported fast reaction between $SO_2$ and $NaHCO_3$ at 64.4°C (148°F) proceeds without any intermediately formed anhydrous $Na_2CO_3$.

Figure 9 depicts the $SO_2$ absorption achieved in the sand bed, expressed as conversion of $Na_2O$, after one hour, as a function of the relative humidity using various $NaHCO_3$ samples as sorbents. The difference in results between the various samples of $NaHCO_3$ is noteworthy, and is probably related to differences in surface area or other particle characteristics. However, a measurable quantity identifying these differences seems needed.

In summary, the relative humidity is less critical to $SO_2$ absorption by $NaHCO_3$ at low temperature than is $Ca(OH)_2$. The reaction seems to be first order with respect to both $SO_2$ and sorbent. Based on what has been observed here, a mechanism involving the release of $CO_2$ during the reaction of $SO_2$ with $NaHCO_3$ seems best to explain the high reactivity of $NaHCO_3$ without any "blinding" effects.

#### Results Using Calcium Carbonate as Sorbent

Tests using pure reagent grade calcium carbonate, $CaCO_3$, (Fischer C-64) and gas relative humidities in the range 40-70 percent ($\Delta t_s$ approx. 17-7°C (30-12°F)) revealed no $SO_2$ absorption in the sand bed reactor. $SO_2$ absorption by limestone under dry conditions has been reported by others to be enhanced by use of deliquescent salt additives, specifically $CaCl_2$ [5, 6]. The additive enhancement of the sorbent has usually been done by mixing the sorbent with an aqueous solution of the additive followed by drying of the mixture. In the present work, however, the sorbent and additive were mixed dry to exclude any effect of specific sorbent pretreatment on the results obtained in the sand bed reactor.

The additive $CaCl_2 \cdot 2H_2O$ was mixed with the sorbent $CaCO_3$ in the amounts of 0.1 and 0.2 g, respectively, per 1 g sorbent. The effect of the additive on the $SO_2$ absorption measured in the sand bed was significant. Adding $CaCl_2 \cdot 2H_2O$ to $CaCO_3$ in the amount of 0.1 g/g (approximately 7 mol percent) resulted in the definite reaction of $SO_2$ with $CaCO_3$ at 70 percent relative humidity (about 0.1 mol $SO_2$/mol $CaCO_3$ after one hour); however, using 0.2 g/g (approximately 13.5 mol percent) resulted in a $SO_2$ absorption at a magnitude similar to that observed earlier using pure reagent grade $Ca(OH)_2$ at the same conditions (about 0.2 mol $SO_2$/mol $CaCO_3$ after one hour). These results become even more noteworthy as the reaction of $SO_2$ with $CaCO_3$ gave a constant $SO_2$ removal efficiency across the sand bed throughout the testing period, similar to that described above using $NaHCO_3$ as sorbent (Figure 7), but different from that seen with $Ca(OH)_2$ (Figure 2). These observations indicate that the significant reaction inhibiting effect with sorbent conversion ("blinding") which

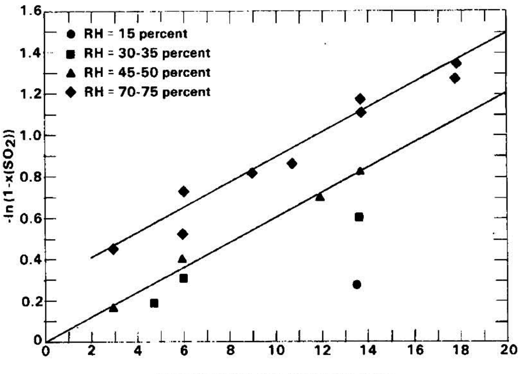


Figure 8. Logarithmic plot of $SO_2$ removal using $NaHCO_3$ as sorbent 64.4°C (148°F), 500-1000 ppm $SO_2$.

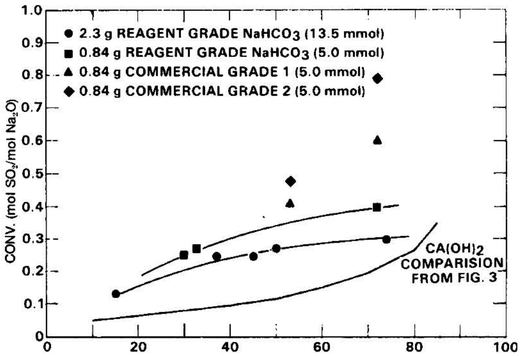


Figure 9. Conversion of $NaHCO_3$ with $SO_2$ (1 hour) 64.4°C (148°F), 500 ppm $SO_2$.

was assessed earlier using $Ca(OH)_2$ as sorbent, does not seem to exist using $CaCl_2$-enhanced limestone. The reaction is constantly proceeding, its rate decreasing only with the depletion of $CaCO_3$ sorbent.

A test matrix using 0.2 g $CaCl_2 \cdot 2H_2O$ per 1 g $CaCO_3$ and 70 percent relative humidity of 64.4°C (148°F) was performed with varying inlet $SO_2$ concentration, amount of $CaCO_3$ sorbent, and amount of sand as test parameters. The results, depicted in Figure 10, suggested that:

1. $SO_2$ absorption increases proportionally with the amount of sorbent.
2. $SO_2$ absorption increases with the $SO_2$ concentration up to approximately 1000 ppm for most conditions tested.
3. The amount of sand used in the bed does not have any significant impact on the amount of $SO_2$ absorbed. (Only at the conditions where the $SO_2$ concentration and sorbent amount were at their maximums might an impact of the total quantity of sand also be detectable.)

These results do not support a single mechanism as rate controlling for $SO_2$ removal at the different test conditions.

Relative humidity is very critical to the degree of $SO_2$ removal which is achievable (also explaining some scatter observed in the above results). Lowering the relative humidity from 70 percent ($\Delta t_s$ approximately 7°C (12°F)) to 50 percent ($\Delta t_s$ approximately 13°C (24°F)) stops virtually all reaction of $SO_2$ with $CaCO_3$. Raising the dry bulb temperature from 64.4°C (148°F) to 74.4°C (166°F) also rapidly decreases the $SO_2$ removal, corresponding to lowering the relative humidity from 70 to 50 percent. Only by raising the wet bulb temperature correspondingly to restore the relative humidity could high $SO_2$ absorption be maintained (Figure 11).

In summary, the theory of a deliquescent salt, $CaCl_2$, generating a liquid phase for $SO_2$ reaction with $CaCO_3$ [5] agrees well with test results noted here. These results imply that a steady state $SO_2$ removal rate can be maintained across the sand bed reactor, unlike the reaction of $SO_2$ with $Ca(OH)_2$ where the reaction rate decreased with time ("blinding").

A few tests performed using NaCl instead of $CaCl_2$ as an additive to limestone revealed no reaction between $SO_2$ and $CaCO_3$. In terms of the above conclusion, this would indicate that the less hygroscopic NaCl (i.e., less affinity for water) does not generate sufficient liquid phase on the particle surface for the dissolution and reaction of $CaCO_3$ with $SO_2$.

Several commercial limestones [Fredonia (Kentucky) and aragonite] have been tested with $CaCl_2$ as the additive and samples of two different particle sizes (all particles minus 325 mesh or all particles in the range 200-325 mesh). The results shown in Figure 11 portray the minus 325 mesh sample of Fredonia (a calcite) to react somewhat faster with $SO_2$ at 70 percent relative humidity than did reagent grade $CaCO_3$. This might be attributed to the higher specific surface area of the finer particles. For aragonite a significantly higher $SO_2$ absorption rate occurred than for either of the tested calcites: the difference was probably related to the different crystal structure or surface shape. Significant $SO_2$ was also removed with argonite at lower relative humidity (40-50 percent relative humidity, $\Delta t_s$ approximately 17-12°C (30-22°F)), especially with the fine particulate fraction (minus 325 mesh) sample of sorbent. Results of a few tests using aragonite without additive enhancement are also presented in Figure 11. Clearly, some $SO_2$ absorption was achieved at high relative humidity, which seems to confirm that the specific sorbent crystal or surface characteristics might be as important for high $SO_2$ removal as the increased liquid phase obtained by addition of a deliquescent salt.

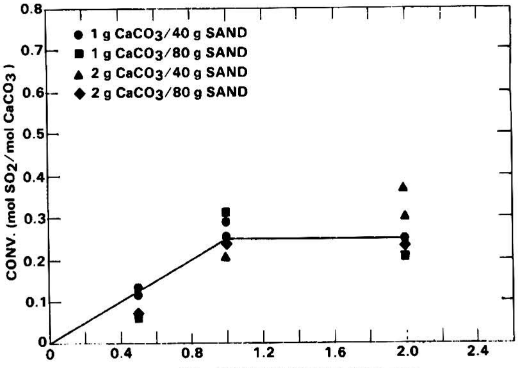


**Figure 10. Conversion of chloride enhanced $CaCO_3$ with $SO_2$ (1 hour)**
**0.2 g ($CaCl_2 \cdot 2H_2O$)/g $CaCO_3$**
**64.4°C (148°F), RH = 70 percent.**

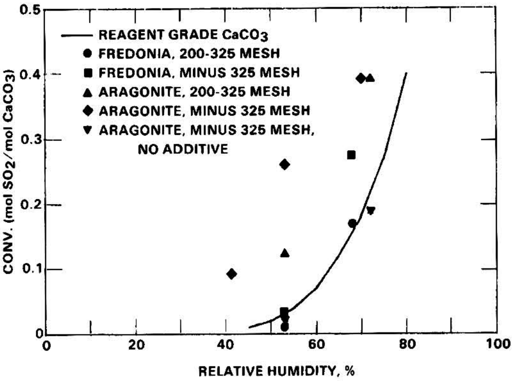


**Figure 11. Conversion of various Cl enhanced $CaCO_3$ with $SO_2$ (1 hour)**
**2 g $CaCO_3$, 0.2 g ($CaCl_2 \cdot 2H_2O$)/g $CaCO_3$**
**64.4°C (148°F), 1000 ppm $SO_2$.**

The last test series to be reported here used sodium nitrate, $NaNO_3$, and calcium nitrate, $Ca(NO_3)_2$, as additives to reagent grade $CaCO_3$ sorbent, and also revealed quite high $SO_2$ absorption in the sand bed when operating at high relative humidity (70 percent relative humidity, $\Delta t_s$ approximately 7°C (12°F)). Moreover, use of both additives revealed a constant $SO_2$ removal across the sand bed throughout the testing period, similar to that described above for $CaCl_2$ added to $CaCO_3$. A "blank" test using only $NaNO_3$ in the sand bed showed no absorption of $SO_2$ at similar conditions, suggesting that only a reaction between $SO_2$ and $CaCO_3$, enhanced by the nitrate compound, could explain the results. The results of a small test matrix aimed at evaluating the effects of the amount of additive used and the $SO_2$ concentration are shown in Figure 12. Surprisingly, these results showed that, for given test conditions, there seems to be an optimum ratio of additive to sorbent for maximum absorption of $SO_2$ by $CaCO_3$. Recalling the previous discussion of a liquid phase on the particle surface, this indicates that a specific ratio of $SO_2$ to $NO_3-$ in the liquid phase results in the highest dissolution rate for $CaCO_3$. While this effect cannot be explained at this point, it is noted that a similar "$SO_x/NO_x$ ratio" has been reported to play a role for simultaneous $SO_x/NO_x$ removal in a spray dryer/baghouse process [*10*].

The $SO_2$ conversion achieved in the sand bed in tests using nitrate additives could show some effect of the time used for "conditioning" the sorbent sample. Also, an increasing $SO_2$ removal efficiency across the sand bed during the testing period could sometimes be observed. These observations suggest that a time factor related to achievement of equilibrium for this specific system might

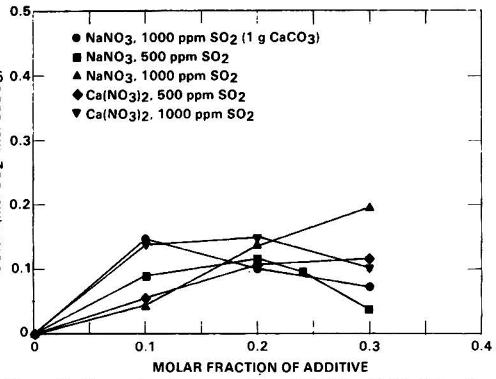


**Figure 12. Conversion of nitrate enhanced $CaCO_3$ with $SO_2$ (1 hour) 2 g $CaCO_3$, 64.4°C (148°F), RH = 70 percent.**

be of importance for the reaction performance.

Finally, some tests with relative humidity and dry bulb temperature as parameters for the $CaCO_3$/nitrate system were also made, but the results were similar to those observed with $CaCl_2$ added to $CaCO_3$. Thus, the relative humidity (or approach to saturation), not the actual temperature, seems to control the $SO_2$ absorbed in the sand bed.

## CONCLUSIONS

- The sand bed reactor has been developed as a useful tool for studying dry sorbent reactions with $SO_2$ at low temperatures.
- Hydrated limes react with $SO_2$ in the temperature range 55-75°C (130-166°F) with the conversion increasing markedly with the gas relative humidity. This agrees with pilot and full-scale dry scrubber test work showing $SO_2$ removal to increase with decreasing approach to saturation.
- At some conditions the lime conversion can be increased 20-30 percent by using 5-10 mol percent salt additives.
- The $SO_2$/lime reaction is inhibited with conversion of the sorbent, probably due to ash buildup on the particle surface ("blinding"). The implication is that a process using recycle of lime sorbent would require some "reactivation" to remove this ash layer to achieve high lime utilization.
- Sodium bicarbonate efficiently absorbs $SO_2$ at 65°C (148°F), but the absorption increases less with increasing gas relative humidity than seen with $Ca(OH)_2$ sorbent. This indicates that a soda based dry scrubber would be less sensitive to changes in approach to saturation.
- The reaction between $SO_2$ and $NaHCO_3$ proceeds without any "blinding." This suggests that very high sorbent utilization can be achieved on a soda based dry scrubber by increasing sorbent residence time in the gas stream.
- Normal $CaCO_3$ does not react with $SO_2$ in the sand bed reactor, but the use of additives such as $CaCl_2$, $NaNO_3$, and $Ca(NO_3)_2$ significantly enhances the reaction at high relative humidity.
- Higher $SO_2$ absorption can be achieved using fine particulate $CaCO_3$ as sorbent and by using aragonite instead of calcite.
- The reactions of $SO_2$ with additive enhanced $CaCO_3$ do not indicate any "blinding" of sorbent with conversion.
- These results suggest that $CaCO_3$ with additive can be used in lieu of hydrated lime in a dry scrubbing system when operating with a low approach to saturation. Increased residence time of sorbent in the fabric filter using dry recycle of sorbent or extending time intervals between cleaning cycles can be expected to lead to higher sorbent utilization.

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**Claus Jorgensen** is a Project Engineer for Acurex Corporation. He is technically responsible for dry FGD pilot plant and bench scale testing and the development of new processes such as high sulfur spray absorption and dry injection using enhanced sorbents. Prior to joining Acurex he worked for approximately five years for A/S Niro Atomizer, Copenhagen, Denmark and Niro Atomizer, Inc., Columbia, Maryland as a Chemical Engineer in process development for the chemical and air pollution control business area. He earned his M.Sc. Ch. Eng. degree at the Technical University of Denmark.

**John C. S. Chang** is a project manager for Acurex Corporation. He has been working on FGD pilot plant testing and FGD process development/evaluation. He earned his B.S.Ch.E. degree at National Taiwan University, M.S. at West Virginia University, and Ph.D. at the University of Texas at Austin.

**Theodore G. Brna** is project manager for EPA's dry flue gas desulfurization (FGD) program and manages EPA's in-house pilot dry and wet FGD pilot plant operations. He received B.S. and M.S. degrees in mechanical engineering from V.P.I. (Virginia Tech) and a Ph.D. from North Carolina State University, where he was a Ford Foundation Fellow. He is a registered professional engineer.

Prior to joining EPA in 1978, he taught at Virginia Tech, served as consultant in the thermal and fluid sciences areas, and was employed by DuPont prior to teaching. He is a member of the American Society of Mechanical Engineers, has held local, regional, and national ASME offices, and recently served as Vice President of Region IV.

# De-Emulsification of Complex Petroleum Emulsions by Use of Microbial Biomass

**N. Kosaric, Z. Duvnjak, and W. L. Cairns**

Chemical and Biochemical Engineering, Faculty of Engineering Science,
The University of Western Ontario, London, Ontario, Canada N6A 5B9

*It has been demonstrated in this laboratory that specific organisms are capable of breaking both o/w and w/o petroleum derived emulsions. Specific bacteria have been selected and have been tested on model (kerosene/water) and on complex field emulsions obtained during enhanced oil recovery trials (w/o) and in tar sands extraction process (o/w).*

*More recent studies involve the use of microbial biomass (sludge) from municipal and refinery waste water treatment processes as the de-emulsifying agents for treatment of these emulsions.*

*The results indicate that either pure microbial cultures or microbial waste biomass can be used to efficiently break industrial emulsions. This approach is a novel application and is a promising alternative to use of chemically synthesized industrial de-emulsifying agents.*

## INTRODUCTION

Complex water-in-oil and oil-in-water emulsions are generated in various petroleum recovery and refining operations. The w/o emulsions are produced as a result of enhanced oil recovery where either steam or water are injected into the reservoir in order to enhance movement of oil from the injection to the recovery well. Very often surfactants are added to the flood with the objective of lowering the surface and interfacial tension between the water and the oil layers within the reservoir. As a result, the recovered oil is in the form of a w/o emulsion. These emulsions are complex in composition and sometimes very stable. The stability of the emulsions is also enhanced by the presence of inorganic particles such as clay.

Prior to further processing of the petroleum phase, the emulsion must be broken and the aqueous layer separated from the (usually heavy) oil. This separation is troublesome and difficult and is presently performed by the use of synthetic de-emulsifying agents or by combination of physico-chemical methods which have a variable success.

Another problem in petroleum recovery represent wastewaters which are generated during the oil handling operations. Tremendous amounts of such waters are produced in the hot water alkaline extraction of bitumen from tar sands. In Canada alone it is estimated that there is more oil *in situ* in tar sands than in all reserves of the Arab Peninsula. In order to separate the oil from the sand (about 15% of oil in tarsand) hot alkali is used. The resulting tailings represent not only a loss of emulsified bitumen (oil-in-water emulsion) but also a tremendous pollution burden. At present, two large companies in Alberta, Syncrude and Suncor, recover about 200,000 barrels (31,800 cubic meters) of synthetic crude per day (Lynn, 1985) by the Clark hot water extraction process (Figure 1).

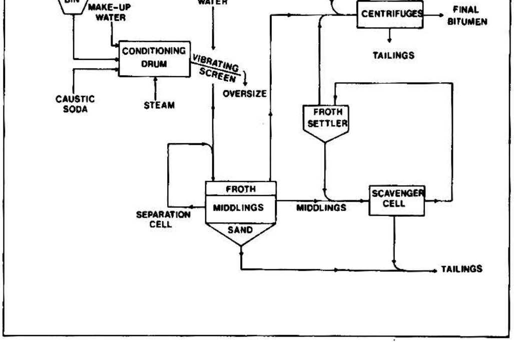


Figure 1. The hot water extraction process for bitumen recovery.

TABLE 1. DE-EMULSIFICATION OF KEROSENE-WATER EMULSIONS BY WHOLE 7-DAY-OLD CULTURES OF BACTERIA GROWN ON HYDROCARBON-CONTAINING MEDIA

| Organism | Half-life (hrs.) of test emulsions stabilized by different surfactants. | | | |
|---|---|---|---|---|
| | Neutral, O/W | Anionic, O/W | Cationic, O/W | Neutral, W/O |
| Control<br>(culture medium) | >200 | >200 | >200 | >200 |
| *Nocardia* | <1 | <1 | <1 | 2 |
| *Rhododoccus* | <1 | 160 | 14 | <1 |
| *Corynebacterium* sp. | <1 | <1 | <1 | 14 |

TABLE 2. THE GENERAL CHARACTERISTICS OF THE FIELD EMULSIONS TESTED

| Field Emulsion | Origin | % Water[1,2] | % Clay[3] | Density g · ml 22°C | Pour Temperature | Other Remarks |
|---|---|---|---|---|---|---|
| P15 liquid | Esso-well head 5:1 liquid/solid | 50.97 (6.1) | 0.20 (0.01) | 0.96 (0.015) | <20°C | Breaks spontaneously in <24 h. |
| solid | | 31.0 (0.12) | 0.20 (0.02) | 0.779 (0.09) | 38°C | |
| K9 liquid | Esso-well head 2.5:1 liq./solid | 74.3 (5.5) | 0.63 (0.06) | 1.0 (0) | <20°C | |
| solid | | 41.3 (0.5) | 1.1 (0.07) | 1.16 (0.19) | 43°C | |
| L15 | Esso-well head | 31.3 (1.1) | 1.66 (0.3) | 1.12 (0.01) | <20°C | |
| R12 | Esso-well head | 10.3 (1.5) | 1.4 (0.2) | 1.22 (0.02) | <20°C | |
| FW15 | Treater sample Esso | 9.3 (1.2) | 3.1 (0.3) | 1.03 (0.9) | <20°C | |
| 1-JB-15-5 | Ath. Bitumen rec. w stream flood | 7.33 (0.8) | 1.2 (0.02) | 0.87 (0.2) | 55°C | |
| 1-JB-15-6 | Ath. bitumen stream flood | 29.3 (2.3) | 0.9 (0.05) | 0.78 (0.12) | 68°C | |
| 1-JB-15-7 | Stream drive Lloydminster | 5.3 (0.9) | 2.03 (0.03) | 0.7 (0.3) | <20°C | |
| 1-JB-15-8 | Combustion Lloydminster | 29.3 (1.9) | 3.07 (0.06) | 0.96 (0.02) | <20°C | |
| 1-JB-15-9 | Combustion Lloydminster | 7.9 (0.7) | 2.5 (0.05) | 0.95 (0.04) | 49°C | |

NOTE: [1] Numbers represent the mean of 3 trials with the standard error in brackets

[2] Dean Start Distillation

[3] Residue remaining after 16h at 500°C

The 1-JB series of emulsions were supplied by AOSTRA.

The amount of tailings, only from the Syncrude operation which mines about 235,000 tons of tar sands/day, is about 208,000 liters per minute. This tremendous quantity of tailings is about 40% larger in volume than the volume

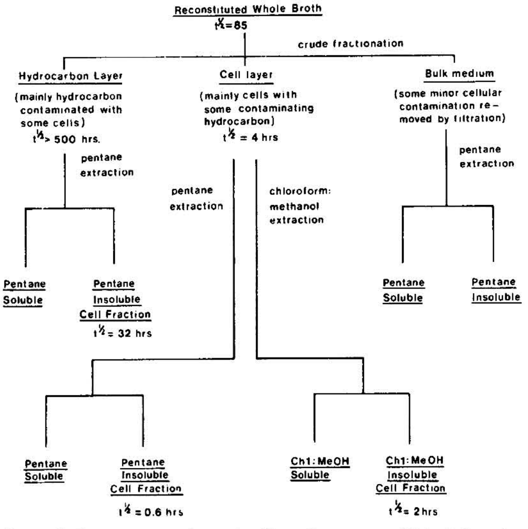
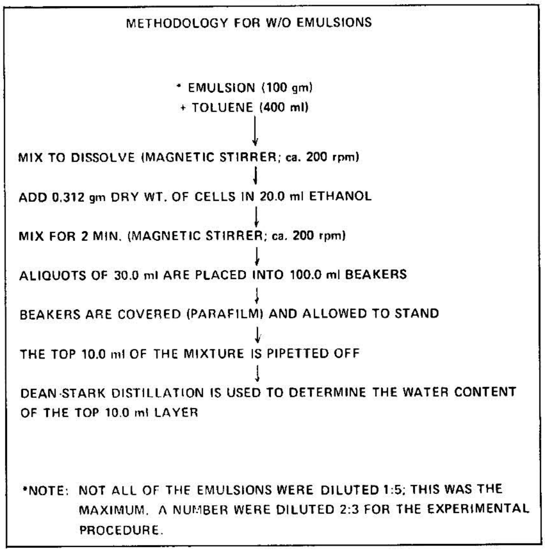


**Figure 2. Fractionation scheme for *Nocardia amarae* with half-lives for each fraction.**



METHODOLOGY FOR W/O EMULSIONS

* EMULSION (100 gm)
+ TOLUENE (400 ml)

MIX TO DISSOLVE (MAGNETIC STIRRER; ca. 200 rpm)

ADD 0.312 gm DRY WT. OF CELLS IN 20.0 ml ETHANOL

MIX FOR 2 MIN. (MAGNETIC STIRRER; ca. 200 rpm)

ALIQUOTS OF 30.0 ml ARE PLACED INTO 100.0 ml BEAKERS

BEAKERS ARE COVERED (PARAFILM) AND ALLOWED TO STAND

THE TOP 10.0 ml OF THE MIXTURE IS PIPETTED OFF

DEAN-STARK DISTILLATION IS USED TO DETERMINE THE WATER CONTENT OF THE TOP 10.0 ml LAYER

*NOTE: NOT ALL OF THE EMULSIONS WERE DILUTED 1:5; THIS WAS THE MAXIMUM. A NUMBER WERE DILUTED 2:3 FOR THE EXPERIMENTAL PROCEDURE.

**Figure 3. Methodology for w/o emulsions.**

METHODOLOGY FOR O/W EMULSIONS

10.0 ml O/W EMULSION
(NO DILUTION)
↓
ADD 500 ppm OF THE BACTERIA TO BE TESTED
↓
VORTEX FOR 5 s.
↓
LEAVE TUBES STANDING, AFTER COVERING WITH PARAFILM
↓
REMOVE UPPER 1.0 ml AND PLACE IN A PRE-WEIGHED ALUMINUM WEIGHING DISH
↓
LEAVE AT 105° C FOR 12 HOURS
↓
MEASURE THE WEIGHT
(GIVES THE AMOUNT OF OIL REMAINING IN UPPER LAYER)

**Figure 4. Methodology for o/w emulsions.**

of the mined oilsand, which also represents a difficult disposal problem. Large lagoons occupying an area of about 12 square miles have been established to accept these tailings.

The oil in the tailings is present as an o/w emulsion which is stabilized by clay particles. In addition to oil, these tailings also contain a significant amount of heavy metals such as zirconium, titanium and some rare elements which recovery is of commercial interest (Ityokumbul et al, 1985a, 1985b, 1986).

The above two types of petroleum field emulsions (w/o and o/w) have been investigated for de-emulsification by selected microbial systems and by waste aerobic and anaerobic sludges.

### Studies with model emulsions

Preliminary data on microbial de-emulsification of oil and water mixtures have been performed in laboratories by use of simple model kerosene-water emulsions. The emulsions were prepared by use of synthetic emulsifiers and potent microbes were isolated and selected (Cooper et al, 1980, Cairns et al, 1983). The results of these preliminary tests are shown in Table 1.

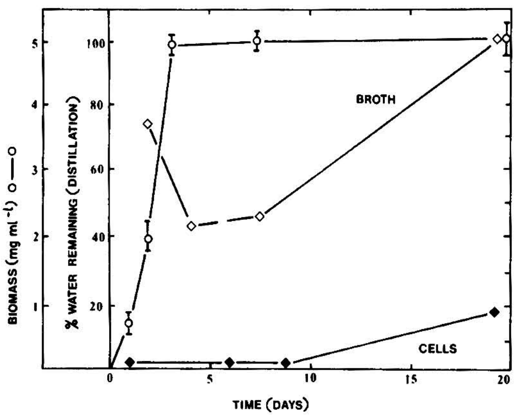


**Figure 5. The de-emulsifying ability of *N. amarae* cells and broth for w/o emulsions.**

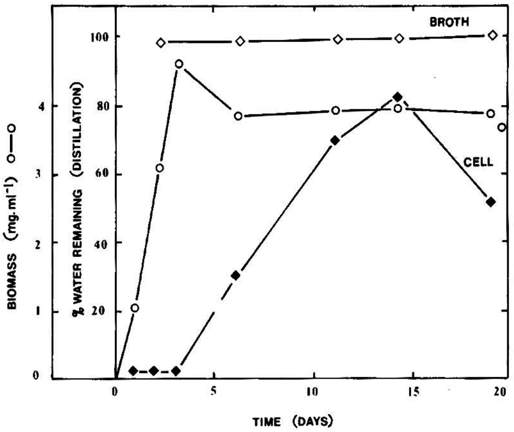


**Figure 6. The de-emulsifying activity of *C. petrophilum* cells and broth for w/o emulsions.**

It is obvious from this Table that some microbes do possess the ability to efficiently and quickly de-emulsify o/w and w/o emulsions. This encouraged us to direct our efforts to handling complex field emulsions.

Through the financial assistance by the Alberta Oil Sands Research Authority (AOSTRA) we were able to engage in a systematic study of this microbiological approach in de-emulsifying these complex systems. It was also found in previous studies, that the cell biomass was responsible for the de-emulsification activity. This is evident from the data as presented in Figure 2.

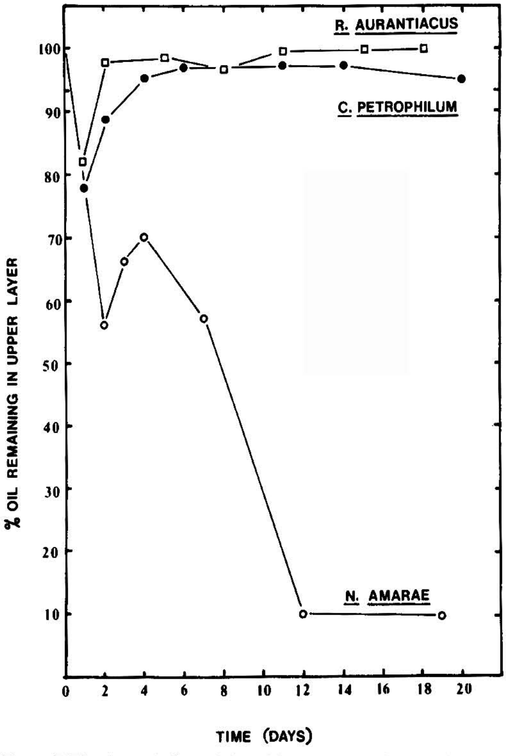


**Figure 7. The de-emulsifying ability of *R. aurantiacus*, *C. petrophilum* and *N. amarae* on an oil-in-water emulsion (K9).**

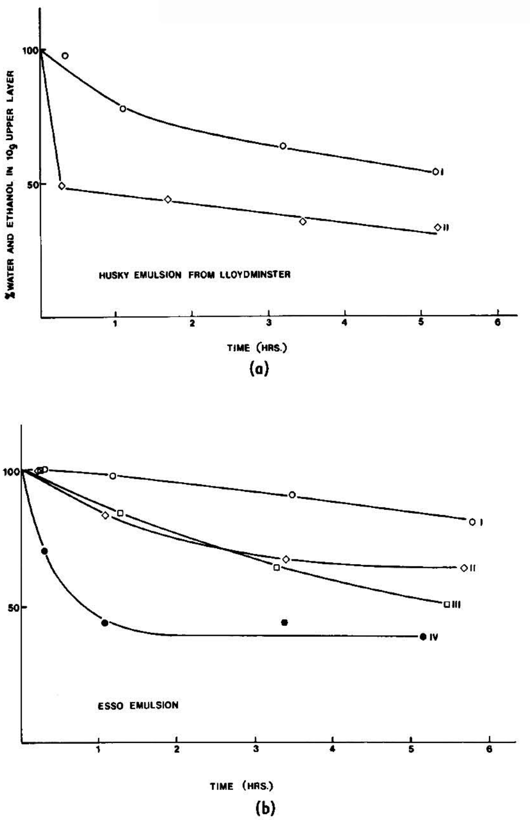


Figure 8. De-emulsification of Husky and Esso emulsions with sludge from an anaerobic digestor.

a) Each system contains (for Husky emulsion)
150 g emulsion + 50 ml toluene and in:
I + 20 ml ethanol
II + 0.368 (d.w.) sludge in 20 ml ethanol

b) Each system contains (for Esso emulsion)
150 g emulsion + 60 ml toluene and in:
I + 20 ml ethanol
II + 0.0970 g (d.w.) sludge in 20 ml ethanol
III + 0.2968 g (d.w.) sludge in 20 ml ethanol
IV + 0.6837 g (d.w.) sludge in 20 ml ethanol

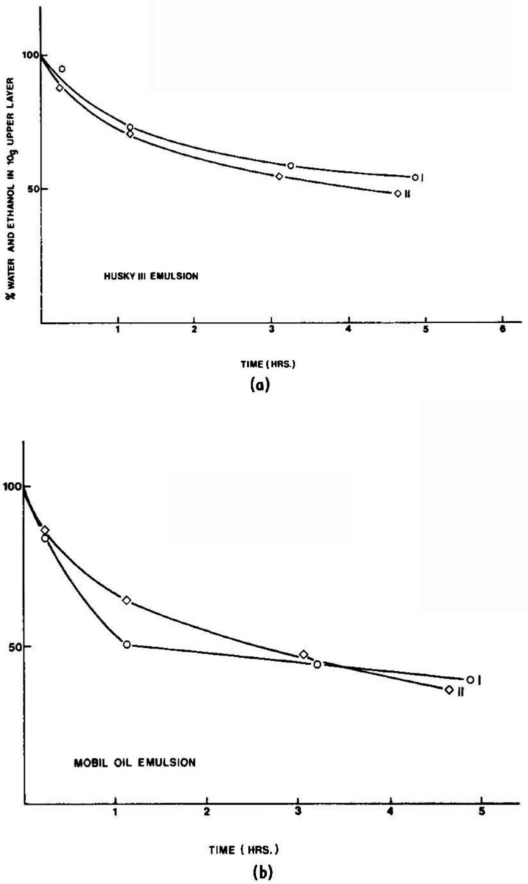


Figure 9. De-emulsification of Husky III and Mobil Oil emulsions with anaerobic granules from UASBR.

a) Each system contains (for Husky III emulsion)
150 g emulsion + 50 ml toluene in:
I + 20 ml ethanol
II + 0.499 g (d.w.) granules in 20 ml ethanol

b) Each system contains (for Mobil Oil emulsion)
150 g emulsion + 50 ml toluene in:
I + 20 ml ethanol
II + 0.500 g (d.w.) granules in 20 ml ethanol

**Studies with field emulsions**

A great number of field emulsions were obtained from AOSTRA and from various petroleum companies for microbial de-emulsification studies. The list of some typical emulsions is given in Table 2 and the methodology used in the testing of w/o and o/w emulsions is shown in Figures 3 and 4 respectively.

It was interesting to observe [*1*, *4*] that the de-emulsification by selected bacteria (*Nocardia amarae* and *Corynebacterium petrophilum*) depended very much on the age of the culture. Younger cells were very active in de-emulsifying w/o emulsions while older cells efficiently de-emulsified o/w emulsions. (Figures 5, 6 and 7).

It was also shown in these experiments that the efficiency of de-emulsification depended upon a number of factors such as:

- Source of the emulsion tested
- Nature and chemical composition of the emulsion
- Hydrocarbons in the oil phase
- Presence of clay or other inorganic particles
- Quantity of cells used
- Nature of the cell surface
- Age of the cells
- Media used for cell growth
- Percent of water in the emulsion

**Studies with microbial biomass (sludge)**

The ultimate objective in the above studies was to evaluate this microbial application in a large scale industrial operation. For any large scale use, the microbial de-emulsifier must be available in large quantity and at a low price. It was therefore of interest to investigate whether the production of the de-emulsifying agent could be accomplished by use of microbial biomass which may even be available in large quantity as a waste material.

Sludges from municipal or industrial wastewater treatment facilities would be excellent candidates for such applications. Waste sludges from biological treatment plants do actually represent a complex mixed microbial cell population. Their disposal is usually a problem and their utilization for useful purposes is limited. If these sludges could de-emulsify complex petroleum emulsions, a very cheap de-emulsifying agent would be available to be used

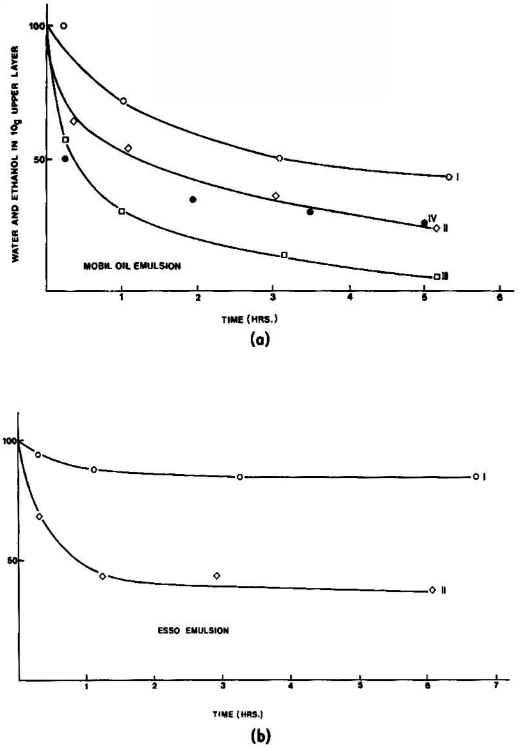


Figure 10. De-emulsification of Mobil Oil and Esso emulsions with municipal aerobic sludge (flotation stage).

a) Each system contains (for Mobil Oil emulsion)
150 g emulsion + 50 ml toluene in:
I + 20 ml ethanol
II + 0.508 g (d.w.) flotation crude in 20 ml ethanol
III + 1.002 g (d.w.) flotation crude in 20 ml ethanol
IV + 1.496 g (d.w.) flotation crude in 20 ml ethanol
b) Each system contains (for Esso emulsion)
150 g emulsion + 60 ml toluene and in:
I + 20 ml ethanol
II + 0.600 g (d.w.) flotation crude in 20 ml ethanol

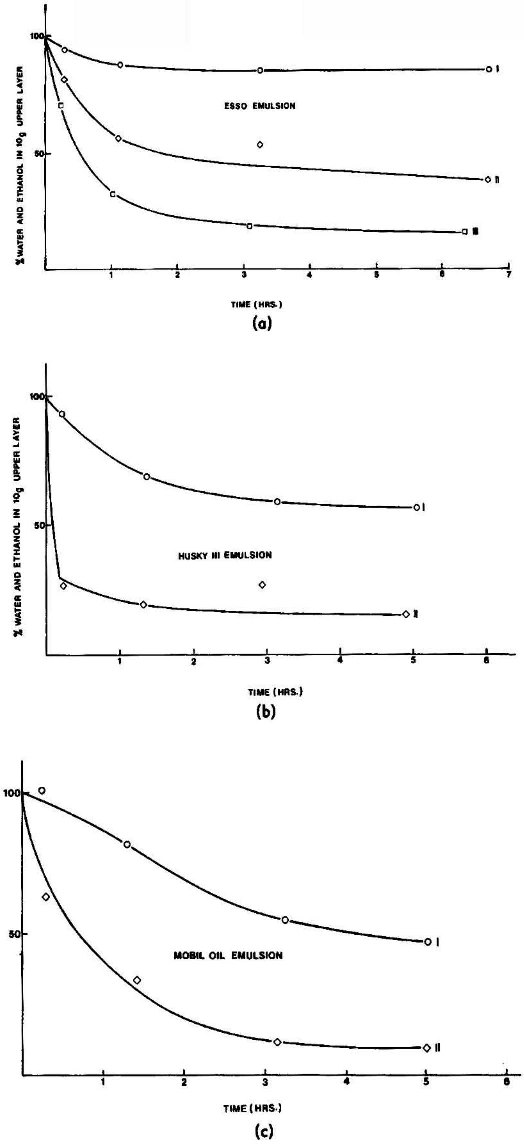


Figure 11. De-emulsification of Esso, Husky III and Mobil Oil emulsions with municipal aeorbic sludge (aeration stage).

a) Each system contains (for Esso emulsion)
150 g emulsion + 60 ml toluene and in:
I + 20 ml ethanol
II + 0.504 g (d.w.) sludge in 20 ml ethanol
III + 1.000 g (d.w.) sludge in 20 ml ethanol
b) Each system contains (for Husky III emulsion)
150 g emulsion + 50 ml toluene and in:
I + 20 ml ethanol
II + 0.741 g (d.w.) sludge in 20 ml ethanol
c) Each system contains (for Mobil Oil emulsion)
150 g emulsion + 50 ml toluene and in:
I + 20 ml ethanol
II + 0.742 g (d.w.) sludge in 20 ml ethanol

on a large scale. Results show that sludges can be used for this purpose.

The following sludges were investigated for this use:

a) Sludge from a conventional municipal anaerobic digester.
b) Non dispersed microbial aggregates from an Upflow Sludge Blanket Reactor.
c) Aerobic sludge from a municipal activated sludge treatment plant (harvested from the aerator).
d) Aerobic sludge from the same plant (c) harvested from the flotation stage.
e) Aerobic sludge from an activated sludge process of a petroleum refinery (ESSO).

The sludges were autoclaved at 120°C for 30 minutes and were applied to the emulsions according to the procedure as shown in model de-emulsification systems. Figures 8-12 show the results obtained.

As it can be seen from these results, certain sludges can be used to de-emulsify complex w/o and o/w emulsions. Aerobic sludges were more active than anaerobic. The de-emulsification was accomplished without any specific pretreatment of the sludges except for their heat sterilization. This approach opens new avenues for:

a) Utilization of aerobic and anaerobic sludges.
b) Cheap de-emumlsification of complex petroleum/water emulsions.

Present work is focused on process optimization, additional sludge pretreatment and establishment of scaled-up process parameters.

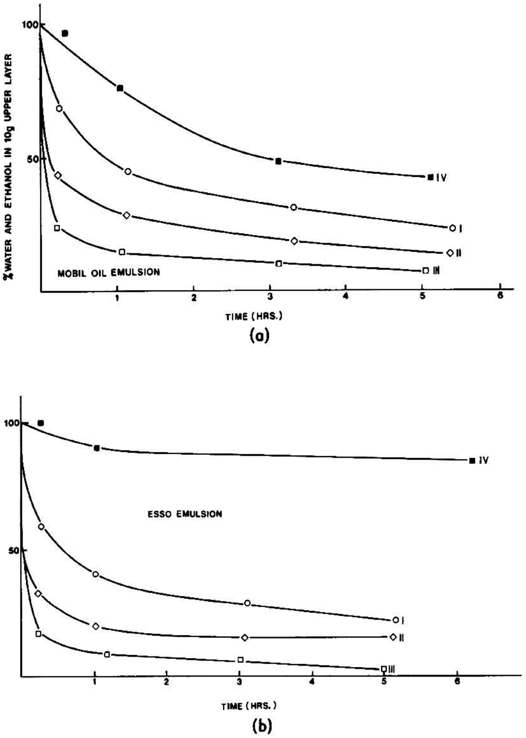


**Figure 12. De-emulsification of Mobil Oil and Esso emulsions with Esso aerobic sludge.**

**a) Each system contains (for Mobil Oil emulsion)**
**150 g emulsion + 50 ml toluene and in:**
**I + 1 g (d.w.) sludge in 20 ml ethanol**
**II + 3 g (d.w.) sludge in 20 ml ethanol**
**III + 6 g (d.w.) sludge in 20 ml ethanol**
**IV + 20 ml ethanol (control from November 29, 1984)**
**b) Each system contains (for Esso emulsion)**
**150 g emulsion + 60 ml toluene and in:**
**I + 1 g (d.w.) sludge in 20 ml ethanol**
**II + 3 g (d.w.) sludge in 20 ml ethanol**
**III + 6 g (d.w.) sludge in 20 ml ethanol**
**IV + 20 ml ethanol (control from December 13, 1984)**

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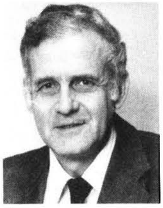

**Professor Naim Kosaric** was boen in Sarajevo, Yugoslavia and obtained a Dip. Ing. in Chemical Engineering from the University of Zagreb, Yugoslavia, and a Ph.D. in Biochemistry from the University of Western Ontario, Canada, where he has been a Professor since 1966. His specialty field is in Biochemical and Food Engineering Industrial Wastewater Treatment and he is a member of the Association of Professional Engineers of Ontario as well as AIChE, CIFST, NSC, CSChE and CIC. A consultant for many industries and government he also has over 100 refereed publications.

# The Pilot-Scale Demonstration of the MODAR Oxidation Process for the Destruction of Hazardous Organic Waste Materials

**Carl N. Staszak, Kenneth C. Malinowski**
CECOS International, Inc., 2321 Kenmore Avenue, Buffalo, New York 14207
and

**William R. Killilea**
MODAR, Inc., 14 Tech Circle, Natick, Massachusetts 01760

*CECOS International, Inc., a hazardous waste treatment and disposal firm headquartered in Buffalo, New York, and MODAR, Inc. of Houston, Texas, conducted a field, pilot-scale demonstration of the MODAR Oxidation Process for the destruction of hazardous organic waste materials in 1985. The MODAR Oxidation Process utilizes water at conditions above its critical point (647K and 22.1 MPa) as the reaction medium for the oxidation of organic materials. The products of this oxidation reaction, for a typical organic material, are carbon dioxide and water. Any halogen present as part of the organic matrix is converted to its halo-acid form. Two waste streams were destroyed in the field tests. These were an aqueous-based waste contaminated with several organic EPA priority pollutants, and an organic transformer dielectric fluid contaminated with polychlorinated biphenyls (PCBs). In both tests, water constituent concentrations in liquid and gas process effluents were below analytical detection limits. Destruction efficiencies based on influent concentrations and the reported detection limits were greater than "four nines". The results of the demonstration have shown the process' ability to destroy toxic and persistent organic contaminants in liquid wastestreams without producing hazardous by-products.*

## INTRODUCTION

During the Summer of 1985, CECOS International, Inc. of Buffalo, New York, and MODAR, Inc. of Houston, Texas, conducted a field, pilot-scale demonstration of the MODAR Oxidation Process for the destruction of hazardous organic waste materials. The demonstration, performed at CECOS' Niagara Falls, New York Hazardous Waste Treatment and Disposal Facility, employed a skid-mounted oxidation unit, having a nominal organic material flow capacity of 190 liters per day, for the destruction of two waste streams. These streams were an aqueous-based waste and an organic dielectric fluid containing polychlorinated biphenyls (PCBs).

The MODAR process for hazardous waste destruction uses water in its supercritical state (above 647K and 22.1 MPa) as the process medium for carrying out the destruction of organic materials by oxidation. Key to the success of the process is the fact that gases, including oxygen, and organic substances are completely soluble in supercritical water, whereas inorganic salts exhibit greatly reduced solubilities under process conditions. Thus, it is possible to carry out oxidation reactions by dissolving organic substances and oxygen in the supercritical medium, thereby bringing them into intimate, single-phase contact at temperatures and molecular densities which allow conventional oxidation reactions to proceed rapidly to completion.

The process provides a method of rendering waste materials into non-hazardous compounds. Organic waste components are converted to carbon dioxide and water with potential recovery of the heat of oxidation, while inorganic components can be separated out as solid salts, and reused or safely discarded. Water, when present in the waste matrix, is recovered in a highly purified form. The wastes are treated in an enclosed system so that the escape of pollutants to the environment is a remote possibility.

Bench and pilot-scale laboratory work performed by MODAR confirmed the effectiveness of the process on both pure chemicals and synthesized mixtures of chemicals. However, its applicability to "real world" hazardous waste materials was still undemonstrated at the pilot-scale. Through MODAR's affiliation with CECOS, a pilot-scale test on toxic waste material was envisioned, and ultimately realized. This paper describes the MODAR Oxidation Process, the objectives and performance of the test program, and the results of the demonstration.

## PROCESS DESCRIPTION

A schematic flow sheet for the MODAR process as applied to liquid wastes is presented in Figure 1.

The process consists of the following steps:

### Feed

1. Organic waste materials in an aqueous medium are pumped from atmospheric pressure to the pressure in the reaction vessel.
2. Oxygen, stored as a liquid, is pumped to the pressure of the reaction vessel and then vaporized. Alternatively, air can be compressed to system pressure and metered into the reaction vessel.
3. Feed to the process is controlled to an upper limit of heating value of 4.2 MJ/kg by adding dilution water or blending higher heating value waste material with lower heating value waste material prior to feeding to the reactor.
4. When the aqueous waste has a heating value below 4.2 MJ/kg, fuel may be added in order to utilize a cold feed to the oxidizer.
5. Optionally, for wastes with heating value below 4.2 MJ/kg, a combination of preheat by exchange with process effluent and fuel addition, or preheat alone may be used.
6. When organic wastes contain heteroatoms which produce mineral acids, and it is desired to neutralize these acids and form appropriate salts, caustic is injected as part of the feed stream.
7. A recycle stream of a portion of the supercritical process effluent is mixed with the feed streams to raise the combined fluid to a high enough temperature to ensure that the oxidation reaction goes rapidly to completion.

### Reaction and Salt Separation

1. Because the water is supercritical, the oxidant is completely miscible with the solution (i.e., the mixture is a single, homogeneous phase). Organics are oxidized in a controlled but rapid reaction. Since the oxidizer operates adiabatically, the heat released by the readily oxidized components is sufficient to raise the fluid phase to temperatures at which all organics are oxidized rapidly.
2. Since the salts have very low solubility in supercritical water, they separate from the other homogeneous fluids and fall to the bottom of the separation vessel where they are removed.

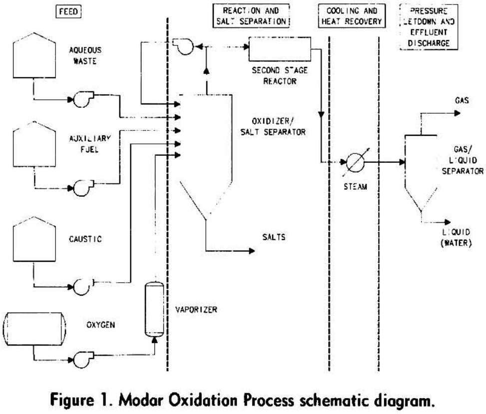

Figure 1. Modar Oxidation Process schematic diagram.

3. The gaseous products of reaction, along with the supercritical water, leave the reactor at its top. A portion of the supercritical fluid is recycled to the oxidizer by a high temperature, high pressure pump. This operation provides for sufficient heating of the feed to bring the oxidizer influent to optimum reactor conditions.
4. The remaining reactor effluent (other than that recycled), consisting of supercritical water and carbon dioxide, is cooled to discharge carbon dioxide and water at atmospheric conditions.

### Cooling and Heat Recovery

1. Most of the heat contained in the effluent can be used to generate steam for use outside the MODAR Process.
2. The heat remaining in the effluent stream can be used for lower level heating requirements or else be dissipated.

### Pressure Letdown

1. The cooled effluent from the process separates into a liquid water phase and a gaseous phase, the latter containing primarily carbon dioxide along with oxygen which is in excess of the stoichiometric requirements (and nitrogen when air is the oxidant).
2. The separation is carried out in multiple stages in order to minimize erosion of valves as well as to optimize equilibria.
3. Salts are removed from the separator as a cool brine through multiple letdown stages and are either dried (and water recovered) or discharged, depending upon operating requirements.

### Process Advantages

The MODAR process has several advantages over conventional processes for waste destruction. These include: very high destruction of organic compounds including chemically-stable materials (such as PCBs); the oxidation can be energy self-sufficient with as little as 2% organic concentration; and excess energy may be easily recovered as steam. The process operates at conditions below which oxides of nitrogen are formed; the MODAR technology is self-scrubbing; and inorganic contaminants such as salts and metals are separated from contaminated waste streams thus substantially reducing waste volumes. It provides for beneficial recovery of valuable components of the waste material, i.e. water for reuse, energy as noted above and in some cases inorganic salts. The MODAR system is closed loop; any process upset shuts the system down and the effluents are contained, not released to the environment.

## PROCEEDINGS

### Permitting

A permit for the temporary operation of the MODAR Oxidation Process at CECOS' Niagara Falls, New York Facility was required by the New York State Department of Environmental Conservation (NYSDEC), and was received from the Department in September, 1984. Formal authorization was requested from the United States Enviornmental Protection Agency (USEPA) for the use of a PCB-contaminated material for research and development purposes. This authorization was received in October, 1984.

Figure 2 shows a plot plan of the installation with the major operating areas identified. The MODAR Oxidation

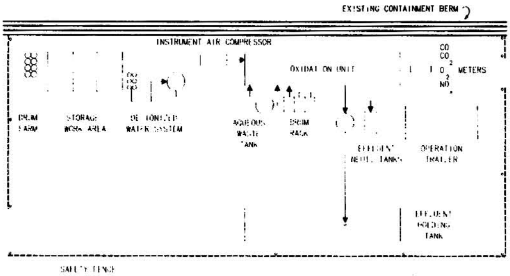

Figure 2. Modar Oxidation Process demonstration plot plan.

Process demonstration unit is skid-mounted and designed to be transportable by truck. The unit measures 12.2 m × 2.6 m × 2.9 m. It has been designed and constructed to meet Class I, Division 2 electrical codes.

The unit's major components, as shown in the schematic of Figure 3, are grouped into modules. The first component is the system air compressor, followed by the stainless steel water reservoir and pump. Next, the aqueous and organic waste modules, consisting of stainless steel holding tanks and pumps, are each surrounded by splash barriers. These components also are separated from the hot zone by a floor-to-ceiling steel bulkhead. Within the hot zone itself, the start-up heaters, reactor, and heat exchangers are contained in Marinite-insulation enclosures. Upon leaving the hot zone, the process stream enters the pressure letdown module containing the liquid-vapor separators and the stainless steel effluent reservoir. Another steel bulkhead separates the letdown modules from the two Hoffmann boxes containing the module's electrical connections. Each Hoffmann box is individually purged with air. The system is designed to process 190 liters of organic, or 950 liters of 10% organic in an aqueous medium, per day with a total throughput to waste ratio of up to 30:1.

#### Inspection and Testing

Following installation of the unit, NYSDEC inspections were performed to ensure permit compliance. The NYSDEC verified that all appropriate safety, health and environmental procedures were in place. They also witnessed a hydrostatic pressure test of all zones of the system.

MODAR subsequently conducted a short term operational test to verify organic destruction by oxidizing isopropyl alcohol (IPA). On-line instrumentation for temperature, pressure, flow, level, and gas and liquid analysis were also checked.

#### Aqueous Waste Destruction Test

The waste destroyed by the process was a dilute isopropyl alcohol stream contaminated with trace quantities of several other pollutants. In order to increase the organic content of the waste, as well as to provide compounds which could be traced for calculation of destruction efficiencies, three organic compounds were added to the organic matrix: 1, 1, 2-trichloroethane, nitrobenzene, and 2-chlorophenol. Table 1 shows the concentrations of the major constituents (except for the IPA) in the synthesized waste.

Since the waste had a total organic carbon (TOC) content of only 1%, it was clear that it was not concentrated enough for the exothermic oxidation reaction to maintain the temperatures necessary for complete oxidation of the organic compounds. For this reason, IPA was fed to the reactor along with the wastewater as a supplemental fuel source. At steady state, the waste oxidation temperature was in the range of 888 to 908K. Approximately 145 operating hours were logged during this phase of the demonstration, and approximately 3400 liters of waste were processed through the unit.

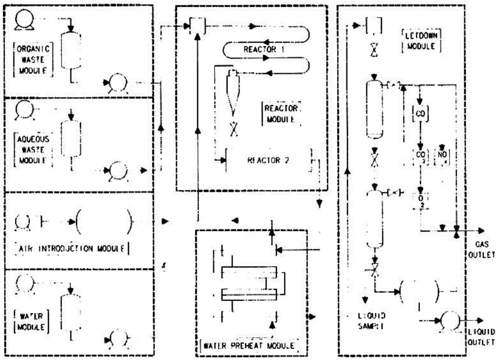

Figure 3. Pilot-scale unit arrangement.

#### Organic Waste Destruction Test

The organic waste destroyed by the unit was a transformer dielectric fluid containing polychlorinated biphenyls. The concentration of the PCBs in the fluid was 1600 mg/L on an Aroclor 1260 basis. This value was used as the basis for all destruction efficiency calculations.

As in the dilute aqueous waste test, the MODAR demonstration unit was started up by heating process air and water. When oxidation of a clean mineral oil, mixed with an appropriate amount of dilution water, raised the operating temperatures to optimal levels, the PCB contaminated oil flow was started. At steady state, oxidation temperatures were in the range of 873 to 897K.

Due to the high endothermic heat of mixing between supercritical water and the compressed air oxidant, the temperature at the reactor inlet was cooler than optimum. For this reason, the rate at which the cold organic waste/dilution water was fed to the unit was cut back to approximately 50% of capacity in order to ensure that the reaction stayed within prescribed oxidation temperatures.

Approximately 95 hours of running time were logged during this phase of the test, bringing the total elapsed running time for the demonstration to 240 hours. A volume of 330 liters of organic waste was oxidized by the unit.

## DEMONSTRATION RESULTS AND DISCUSSION

### Aqueous Waste Test Results

During the course of the steady state run, key performance parameters were monitored by MODAR operators. These parameters included:

1. *Effluent gas carbon monoxide concentration.* Values were always less than 10 ppm. Low carbon monoxide concentrations indicated high waste oxidation efficiency.

TABLE 1. SYNTHESIZED AQUEOUS WASTE COMPOSITION

| Compound | Concentration (ug/L) |
|---|---:|
| 2-chlorophenol | 1,200,000 |
| Nitrobenzene | 1,100,000 |
| 1, 1, 2-trichloroethane | 190,000 |
| Chloroform | 1,000 |
| Carbon Tetrachloride | 590 |
| Total Organic Carbon | 10,300,000 |

2. *Liquid effluent TOC.* The liquid effluent was sampled between the MODAR Demonstration Unit and the 5700 liter effluent tank. TOC was measured by an on-line analyzer. At the conclusion of the dilute aqueous waste run, the effluent composited throughout the entire test was analyzed. This analysis showed the concentration to be less than 1 mg/L.
3. *Liquid effluent chloride concentration.* Organic chlorine, present in such compounds as chlorophenol, was converted to inorganic chloride during supercritical water oxidation. This chloride remained dissolved in the process' liquid effluent and was analytically quantified using a chloride ion electrode.

Waste destruction efficiencies were calculated for the individual hazardous compounds present in the aqueous waste. Table 2 summarizes these calculations. The waste destruction efficiency is defined as:

$$e_d = \frac{M_{fi} - (M_{gi} + M_{li})}{M_{fi}} \times 100\% \qquad (1)$$

where: $e_d$ = destruction efficiency, %
$M_{fi}$ = mass feed rate of component i to the unit, g/min
$M_{gi}$ = mass effluent rate of component i in the gaseous effluent from the unit, g/min
$M_{li}$ = mass effluent rate of component i in the liquid effluent from the unit, g/min

Since all the compounds were found to be either analytically not detected or below the detection limit in both the liquid and gas effluents, the laboratory's standard detection limits have been used as the basis for calculation.

The calculated destruction efficiencies ranged from 99.997% to 99.998% for the major constituents. This should not be construed as the best obtainable destruction efficiency for the process, but is the maximum possible value computed with the fixed influent concentrations and effluent analytical detection limits. In fact, no organic compounds were found above the analytical detection limit in the gas or liquid effluents. Meaningful destruction efficiencies of the minor components can not be determined because of their low waste feed concentration values.

Elemental mass balances were calculated for carbon, oxygen and chlorine. Table 3 lists mass rates and closure of balances.

TABLE 2. WASTE DESTRUCTION EFFICIENCIES MODAR/CECOS DEMONSTRATION

| Contaminant | Feed Rate (g/min × $10^3$) | Liquid Effluent Rate (g/min × $10^6$) | Gaseous Effluent Rate (g/min × $10^6$) | Destruction Efficiency (%) |
|---|---|---|---|---|
| Aqueous Waste Test | | | | |
| 2-chlorophenol | 490 | <9.7 | <4.9 | >99.997 |
| Nitrobenzene | 440 | <5.6 | <2.8 | >99.998 |
| 1, 1, 2-TCE | 77 | <15 | (A) | >99.981 (B) |
| Chloroform | 0.40 | <4.7 | (A) | >99.83 (B) |
| Carbon Tetrachloride | 0.24 | <8.3 | (A) | >96.53 (B) |
| Organic Waste Test | | | | |
| PCB | 91 | <0.31 | <4.4 | >99.9949 |

Notes:
(A) Not analytically recoverable from gas sorbent tubes.
(B) Destruction efficiency based only on liquid analysis.

TABLE 3. ELEMENTAL MASS BALANCE SUMMARIES

| Element | Quantity in (g/min) | Quantity Out (g/min) | Balance Closure % |
|---|---|---|---|
| Aqueous Waste Test | | | |
| Carbon (C) | 44.4 | 42.8 | 96 |
| Oxygen (O) | 296 | 298 | 101 |
| Chlorine (Cl) | 0.196 | 0.200 | 102 |
| Organic Waste Test | | | |
| Carbon (C) | 49 | 48 | 98 |
| Oxygen (O) | 251 | 278 | 111 |
| Chlorine (Cl) | 0.055 | 0.071 | 129 |

### Organic Waste Test Results

Table 2 also summarizes the PCB destruction efficiency based on the test effluent analyses. PCB was not detected in either gas or liquid effluent. A destruction efficiency of 99.995% was calculated, a value which does not represent the maximum obtainable efficiency, but rather a maximum that can be calculated for this instance given the feed concentration and analytical detection limits. Overall elemental mass balances for carbon, oxygen and chlorine for this trial are shown in Table 3.

### CONCLUSIONS

The performance of, and the results from, the MODAR Oxidation Process Demonstration program have shown that:

1. The scale-up of the process from bench-to-pilot-scale was performed effectively and with no loss in process efficiency;
2. The process can be operated in an enclosed manner, thereby preventing inadvertent releases of potentially toxic materials to the environment;
3. The pilot-scale unit can be operated on a long-term basis while maintaining suitable effluent quality;
4. The process can oxidize organic contaminants in an aqueous matrix to non-detectable levels;
5. Similarly, the process can oxidize organic contaminants in an organic liquid matrix, notably PCBs.

It is expected that future cooperation between CECOS and MODAR will result in the possibility of a second demonstration, with the long-term goal being a full-scale installation at one of CECOS' processing facilities.

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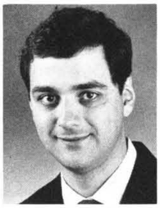
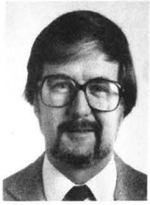


**Carl N. Staszak** is a Research Engineer in the Research and Development Department at CECOS' Corporate office in Buffalo, New York. He holds a B.S. in Chemical Engineering from the State University of New York at Buffalo, where presently he is pursuing a Masters Degree in Business Adminstration. He is also a member of Tau Beta Pi and of the AIChE.



**William R. Killilea,** Manager of Laboratory Operations for MODAR, Inc., is responsbile for process development activities and MODAR's waste testing program. Before joining MODAR in January 1984 he was senior project engineer for Concentration Specialists, Inc. and engineer for Bechtel, Inc. He earned his B.S. in Chemical Engineering from Northeastern University and his S.M. in Chemical Engineering from the Massachusetts Institute of Technology.

# Process Simulation of the Fluidized-Bed Copper Oxide Process Sulfation Reaction

**James T. Yeh, Charles J. Drummond, and James I. Joubert**

U.S. Department of Energy, Pittsburgh Energy Technology Center, P.O. Box 10940,
Pittsburgh, PA 15236

*The Fluidized-Bed Copper Oxide Process is a regenerative process for the simultaneous removal of both sulfur dioxide ($SO_2$) and nitrogen oxides ($NO_x$) from the flue gas of coal-fired boilers. An ideal-flow reactor model for $SO_2$ removal was formulated based on a sulfation reaction kinetics model developed using data from a microbalance reactor. Experimental data obtained from a fluidized-bed reactor having a cross section measuring 1.02 m by 1.22 m (40 in. by 48 in.) were used to validate the model. The variables in the model were systematically varied to predict reactor performance under different operating conditions. The process variables studied were (1) sorbent copper content, (2) reactor bed depth, and (3) reaction temperature. The reactor performance predictions showed that increasing the copper content of the sorbent from 5 percent to 7 percent would lower the required sorbent recirculation rate by 30 percent. The expanded-bed depth in the reactor was also an important parameter. Effective performance of the process can be obtained with lower sorbent recirculation rates if the expanded-bed depth in the reactor is increased.*

## INTRODUCTION

Fluidization is a technique used to bring gaseous reactants at high velocity into intimate contact with solid reactants in order to promote gas-solid heterogeneous reactions. This technique is used to contact a supported sorbent with flue gas in the Fluidized-Bed Copper Oxide Process developed at the Pittsburgh Energy Technology Center (PETC) for the simultaneous removal of sulfur dioxide and nitrogen oxides from coal combustion flue gas.

Research and development of a regenerative fluidized-bed process based on supported copper oxide for the removal of sulfur dioxide and nitrogen oxides has been under way at PETC since the late 1960's. In 1970, McCrea et al. [*1*] reported on the bench-scale evaluation of sulfur dioxide removal using copper-impregnated alumina spheres and presented preliminary design criteria for a process to be used to treat flue gases from a 1000-MW(e) utility boiler burning a 3 percent sulfur coal. A copper-impregnated alumina sorbent, manufactured by UOP, Inc., and containing 6.3 percent by weight of copper, was tested over 200 cycles of sulfur dioxide absorption and regeneration with methane ($CH_4$) in a fixed-bed reactor in the laboratory.

Fluidized-bed testing of the same sorbent material was begun in 1975 using a 15-cm (6-in.)-diameter reactor [2]. These tests were conducted using flue gas generated by the combustion of natural gas. Sulfur dioxide was added to the flue gas to simulate the combustion of high-sulfur coal. During several cycles of absorption and regeneration, ammonia was injected for the simultaneous removal of nitrogen oxides. More tests were conducted to determine (1) the effect of the $NH_3/NO_x$ mole ratio on the simultaneous removal of sulfur dioxide and nitrogen oxides; (2) the amount of unreacted ammonia in the flue gas; (3) the rate of sorbent attrition occurring in the fluidized bed; and (4) the effect of fly ash on reactor performance [3].

Based on the results of this previous research, a fluidized-bed absorber that had a 1.02-m by 1.22-m (40-in. by 48-in.) cross section and was 3.73-m (144-in.) high was designed, fabricated, and installed in a 227-kg/h (500-lb/h) pulverized-coal-fired combustion test facility. A typical flue gas composition generated in this combustion facility is shown in Table 1. A 0.76-m (30-in.)-diameter by 7.92-m (26-ft)-high fixed-bed reactor was also constructed to regenerate the spent sorbent from the absorber. Over 90 percent removal of both sulfur dioxide and nitrogen oxides was obtained in these tests. See Yeh et al. [*4*].

More recently, a continuous test unit integrating absorption and regeneration was constructed. This unit contained a 0.36-m (14-in.)-diameter fluidized-bed reactor. Simultaneous removal of over 90 percent of sulfur dioxide and nitrogen oxides was reported [5, *6*]. In addition, a design and an economic analysis for the application of this process to a 500-MW coal-fired boiler were reported by Drummond et al. [7].

The Shell Flue Gas Treatment Process is based on similar chemistry but uses a cyclic fixed-bed contactor in which the supported sorbent is contained in parallel trays [*8-10*].

TABLE 1. TYPICAL FLUE GAS COMPOSITION GENERATED BY THE 227 KG/H (500 LB/H) COAL-FIRED COMBUSTOR AT THE PITTSBURGH ENERGY TECHNOLOGY CENTER

| | |
|---|---|
| $CO_2$ | 14% |
| $SO_2$ | 2000-3000 ppm[a] |
| NO | 450-950 ppm[b] |
| $NO_2$ | 30 ppm |
| $H_2O$ | 7%-7.5% |
| $O_2$ | 3.6% |
| $N_2$ | 75% |

[a] $SO_2$ was added to the flue gas during certain tests.

[b] Ammonia was added to the primary air during some tests to increase the concentration of NO in the flue gas.

## PROCESS CHEMISTRY

The chemistry of the reactions resulting in the removal of sulfur dioxide and nitrogen oxides from flue gas using copper-impregnated alumina spheres is described below.

$$CuO + SO_2 + \tfrac{1}{2}\,O_2 \rightarrow CuSO_4 \tag{1}$$

$$CuO + SO_3 \rightarrow CuSO_4 \tag{2}$$

Regeneration of the sulfated sorbent can be accomplished by using either hydrogen, carbon monoxide, or methane:

$$CuSO_4 + 2\,H_2 \rightarrow Cu + SO_2 + 2\,H_2O \tag{3}$$

$$CuSO_4 + 2\,CO \rightarrow Cu + SO_2 + 2\,CO_2 \tag{4}$$

$$CuSO_4 + \tfrac{1}{2}\,CH_4 \rightarrow Cu + SO_2 + \tfrac{1}{2}\,CO_2 + H_2O \tag{5}$$

The copper formed in the presence of the reducing gas is immediately oxidized to copper oxide upon contact with the oxygen present in the flue gas:

$$Cu + \tfrac{1}{2}\,O_2 \rightarrow CuO \tag{6}$$

Both copper oxide and copper sulfate act as catalysts for the selective catalytic reduction of nitrogen oxides in the fluidized bed. Ammonia is injected into the flue gas stream before the fluidized-bed absorber to react with the nitrogen oxides as follows:

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \tag{7}$$

$$6\,NO + 4\,NH_3 \rightarrow 5\,N_2 + 6\,H_2O \tag{8}$$

$$2\,NO_2 + 4\,NH_3 + O_2 \rightarrow 3\,N_2 + 6\,H_2O \tag{9}$$

$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O \tag{10}$$

## SULFATION AND REGENERATION KINETICS

Kinetics for the sulfation reaction involving sulfur, oxygen, and copper oxide, and the regeneration reaction involving copper sulfate and methane, hydrogen, or a mixture of carbon monoxide and hydrogen were reported by Yeh et al. [*11*]. The reaction kinetics were derived from data generated by the use of a microbalance reactor (Figure 1). The microbalance reactor is a differential reactor in which the concentration of the gaseous reactant remains constant. A sample plot of the fractional conversion of copper oxide is shown in Figure 2. These curves are exponential with time.

The chemical kinetic rate equation used to describe the sulfation of copper oxide is given below.

$$\frac{dx}{dt} = k(1 - x)p \tag{11}$$

where

$x$ = fractional conversion of copper oxide

$p$ = fractional partial pressure of sulfur dioxide (fraction of total pressure)

$t$ = time, h

$k$ = reaction rate constant, $h^{-1}$.

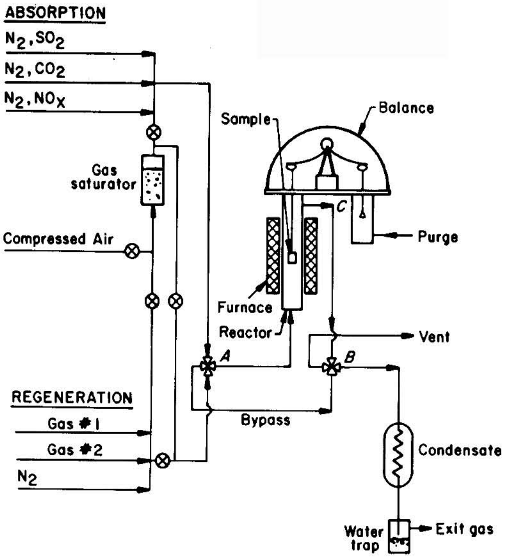


Figure 1. Microbalance reactor used for kinetics study.

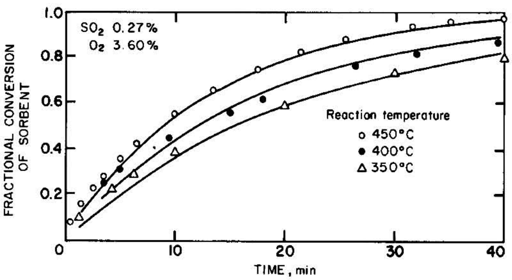


Figure 2. Reaction of $SO_2$ with CuO: Effect of temperature.

Variations of the oxygen concentration in the flue gas were found experimentally to have no effect on the rate of CuO conversion. The rate equation (Equation 11) is linear with both the sulfur dioxide partial pressure in the flue gas (p) and the fraction of unreacted copper oxide $(1 - x)$. The activation energy for the reaction was determined to be 20.1 kJ/mol.

The regeneration of copper by methane, hydrogen, and mixtures of carbon monoxide and hydrogen was also studied using the microbalance reactor. The regeneration reaction was first order with respect to reducing gas concentration for all of the reactants studied. The order of the regeneration reaction with respect to unreacted copper sulfate varied with the reducing gas used. Methane has the lowest reaction rate of the regenerating gases studied (See Figure 3).

## FORMULATION OF A REACTOR MODEL

The kinetic reaction model presented in Equation 11 cannot be used directly for process design, but it is a necessary building block in the formulation of a process model that provides material balance information around the reactor.

The fraction of unreacted CuO can be expressed in terms of the amount of CuO present in the system:

$$(1 - x) = C/C_0 \tag{12}$$

where

$C_0$ = initial mass of CuO per unit mass of $Al_2O_3$

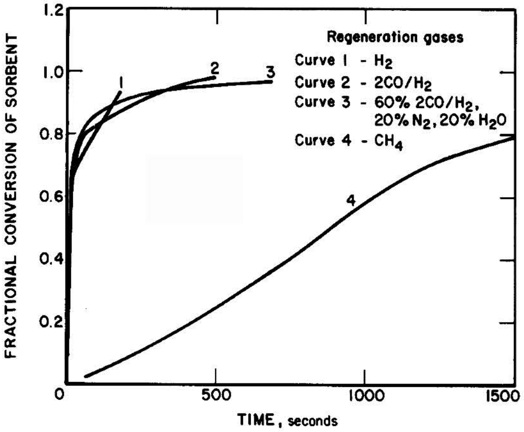
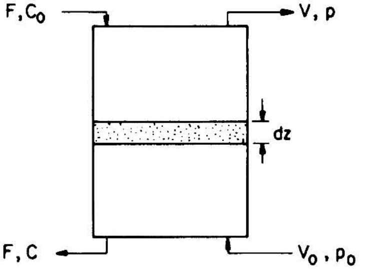


**Figure 3. Regeneration of CuO with different gas at 400°C.**



F = Sorbent Feed Rate, kg $Al_2O_3$/h
$C_0$ = Initial Copper Oxide Content, kg CuO/kg $Al_2O_3$
C = Unreacted Copper Oxide Content, kg CuO/kg $Al_2O_3$
$V_0$ = Inlet Flue Gas Volumetric Flow Rate, $m^3$/h
V = Outlet Flue Gas Volumetric Flow Rate, $m^3$/h
Z = Expanded Bed Depth, m
$p_0$ = Inlet $SO_2$ Concentration, mole fraction
p = Outlet $SO_2$ Concentration, mole fraction

**Figure 4. Differential element of a fluidized-bed reactor.**

C = mass of unreacted CuO per unit mass of $Al_2O_3$

Therefore, the kinetic expression (Equation 11) may be rewritten as follows:

$$-\frac{1}{C_o}\frac{dC}{dt} = kp\left(\frac{C}{C_o}\right) \qquad (13)$$

Now a differential element of a fluidized-bed reactor can be considered (See Figure 4). Before a material balance for this differential element of the reactor can be calculated, the fluidized-bed model most appropriate for the type of reactor under study must be chosen. Several heterogeneous models were evaluated for their ability to simulate the flow regime created by the relatively large fluidized spheres used in this process. The Ideal Flow Model [*12*] was chosen as the basis for the reactor model. The Ideal Flow Model treats the solid particles in the reactor as completely mixed, with the copper oxide concentration being uniform throughout the reactor. A second assumption made by this model is that the fluidized bed behaves like a plug flow reactor in respect to the incoming flue gas.

For a differential height (dZ) of the fluidized bed (See Figure 4), the decrease of $SO_2$ concentration within the finite element can be described by $-d(pV/G)$, moles of $SO_2$ per hour.

Here, V is the outlet flue gas volumetric flow rate ($m^3$/h), and G is the molar volume of gas at the reaction temperature ($m^3$/kg-mole).

The decrease in the quantity of CuO (moles CuO/h) available for reaction can be obtained by rearranging Equation 13:

$$-\frac{dC}{dt}\left(\frac{DA}{M}\right)dZ = \left(\frac{kpCDA}{M}\right)dZ \qquad (14)$$

where

D = fluidized-bed density, kg $Al_2O_3/m^3$ of expanded bed
A = reactor cross-sectional area, $m^2$
M = molecular weight of CuO, kg/kg-mole

One mole of CuO reacts with one mole of $SO_2$. Therefore, in the elemental volume,

$$-d\left(\frac{pV}{G}\right) = \left(\frac{kpCDA}{M}\right)dZ \qquad (15)$$

Now, from the stoichiometry of the reaction (Equation 1), a one mole decrease in the amount of $SO_2$ in the gas phase brings about a decrease in the total amount of gas in the differential element by 1.5 moles. This is expressed in the following equation:

$$\int_{V_0}^{V} dV = 1.5\int_{p_0V_0}^{pV} d(pV) \qquad (16)$$

After integration of Equation 16,

$$V = \frac{(1 - 1.5p_o)\,V_o}{(1 - 1.5p)} \qquad (17)$$

An overall material balance of the reactor shows that the moles of CuO reacted equal the moles of $SO_2$ reacted:

$$F(C_o - C)/M = (p_oV_o - pV)/G \qquad (18)$$

where

F = sorbent feed rate, kg $Al_2O_3$/h

Substitution of Equation 17 in Equation 18 results in the following expression:

$$(C_o - C) = \frac{p_oV_oM}{GF}\left[1 - \left(\frac{1 - 1.5p_o}{1 - 1.5p}\right)\frac{p}{p_o}\right] \qquad (19)$$

And for simplication, Q is defined as follows:

$$Q = \frac{p_oV_oM}{GFC_o} = \frac{\text{moles } SO_2 \text{ feed/h}}{\text{moles CuO feed/h}} \qquad (20)$$

Substituting Q in Equation 19, and rearranging results in the following expression for the amount of unreacted CuO:

$$C = C_o(1 - Q) + C_oQ\left(\frac{1 - 1.5p_o}{p_o}\right)\left(\frac{p}{1 - 1.5p}\right) \qquad (21)$$

Equations 15, 17, and 21 all combined as follows:

$$-d\left(\frac{p}{1 - 1.5p}\right) = \frac{kpDAG}{MV_o(1 - 1.5p_o)}\Bigg[C_o(1 - Q)$$

$$+ C_oQ\left(\frac{1 - 1.5p_o}{p_o}\right)\left(\frac{p}{1 - 1.5p}\right)\Bigg]dZ \qquad (22)$$

Rearranging and integrating Equation 22 results in the following expression:

$$\int_{p}^{p_0} \frac{d\left(\dfrac{p}{1 - 1.5p}\right)}{p\left[C_0(1 - Q) + C_0Q\left(\dfrac{1 - 1.5p_0}{p_0}\right)\left(\dfrac{p}{1 - 1.5p}\right)\right]} = \frac{kDAGZ}{MV_0(1 - 1.5p_0)} \qquad (23)$$

An analytical solution of p as a function of system parameters can be obtained from Equation 23 by integration. In the problem now under study, $p_0$ and p are much less than unity ($p_0$ and p are the initial and outlet $SO_2$ concentrations, respectively, of the fluidized-bed reactor). Therefore, both $(1 - 1.5p_0)$ and $(1 - 1.5p)$ approach unity. This approximation can be used to simplify Equations 17, 21, and 23 as follows:

$$V = V_0 \qquad (24)$$

$$C = C_0(1 - Q) + QC_0(p/p_0) \qquad (25)$$

$$\int_{p}^{p_0} \frac{dp}{p[C_0(1 - Q) + C_0Q(p/p_0)]} = \frac{kDAGZ}{MV_0} \qquad (26)$$

Solving Equation 26 by integration and simplifying the expression results in the reactor model equation:

$$p = \frac{\left(1 - \dfrac{p_0V_0M}{GFC_0}\right)p_0}{\text{Exp}\left[\dfrac{kDAGZC_0}{MV_0}\left(1 - \dfrac{p_0V_0M}{GFC_0}\right)\right] - \dfrac{p_0V_0M}{GFC_0}} \qquad (27)$$

This model predicts outlet $SO_2$ concentration from the fluidized-bed reactor as a function of reactor operating conditions. Because this equation has been derived from a theoretical analysis of the system, the model can be used to predict reactor performance over a wide range of operating conditions.

## RESULTS

### Comparison with Test Data

To verify that the model predicts the performance of the Fluidized-Bed Copper Oxide Process for the removal of sulfur dioxide from flue gas, operating conditions identical to those used in an experimental evaluation of the process in a fluidized-bed reactor [*4*] were used in the model to predict sulfur dioxide removal efficiencies. These predicted removal efficiencies were then compared to the experimental data obtained from the operation of the test unit. The experimental data had been obtained at a scale equivalent to the production of 0.75 MW of electricity using a fluidized-bed reactor having a rectangular cross section measuring 1.02 m by 1.22 m (40 in. by 48 in.). A comparison of experimental data and predicted sulfur dioxide removal efficiencies for 22 test conditions (See Table 2) demonstrates that the model can accurately predict reactor performance. Good agreement between the experimental data and the model predictions was obtained over a wide range of operating conditions. However, the model predictions for the performance of the fluidized-bed reactor during operation with an expanded-bed height of 0.46 m (18 in.) were not as accurate as those for deeper beds (expanded-bed heights of 0.91 m and 1.17 m). For ease of comparison, the data presented in Table 2 are also presented graphically in Figures 5, 6, and 7 (for expanded-bed heights of 1.17 m, 0.91 m, and 0.46 m, respectively).

TABLE 2. RESULTS OF 1.02-M BY 1.22-M (40-IN. BY 48-IN.) FLUIDIZED-BED COPPER OXIDE PROCESS TESTS COMPARED WITH PREDICTED $SO_2$ REMOVAL EFFICIENCIES

| Test No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $SO_2$ Removal, % (Experimental) | 79 | 71 | 90 | 91 | 70 | 81 | 91 | 90 | 67 | 91 | 70 |
| $SO_2$ Removal, % (Predicted) | 84 | 72 | 89 | 90 | 69 | 76 | 89 | 92 | 64 | 98 | 71 |
| Inlet $SO_2$ (Dry), ppm | 2280 | 2280 | 2354 | 2680 | 2680 | 2680 | 3100 | 2100 | 2350 | 2290 | 2950 |
| Bed Temperature, °C | 450 | 460 | 400 | 400 | 465 | 400 | 405 | 420 | 480 | 425 | 425 |
| Sorbent Feed, kg/h | 372 | 290 | 669 | 854 | 351 | 423 | 1053 | 762 | 154 | 453 | 479 |
| Available Cu, % | 3.0 | 3.0 | 2.8 | 3.0 | 3.3 | 3.3 | 2.5 | 3.0 | 5.1 | 5.1 | 2.5 |
| Cu/S Mole Ratio | 0.99 | 0.78 | 1.57 | 1.8 | 0.8 | 0.96 | 1.71 | 1.86 | 0.65 | 2.00 | 0.89 |
| Mole $SO_2$ Removed Per Moles Available Cu | 0.795 | 0.780 | 0.570 | 0.506 | 0.876 | 0.826 | 0.532 | 0.48 | 1.03 | 0.456 | 0.790 |
| Superficial Velocity, m/s | 1.04 | 1.04 | 1.07 | 1.10 | 1.19 | 1.13 | 1.10 | 1.22 | 1.22 | 1.10 | 1.01 |
| Bed Inventory, kg | 614 | 614 | 636 | 641 | 638 | 638 | 696 | 585 | 523 | 469 | 491 |
| Bed Depth, cm | 117 | 117 | 117 | 117 | 117 | 117 | 117 | 117 | 91 | 91 | 91 |

---

°F = 1.8C + 32; lb = 0.4535 kg; $ft^3 = 0.02832\ m^3$; ft/s = 0.3048 m/s.

| Test No. | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $SO_2$ Removal, % (Experimental) | 82 | 91 | 88 | 89 | 90 | 95 | 93 | 90 | 70 | 78 | 84 |
| $SO_2$ Removal, % (Predicted) | 81 | 90 | 85 | 88 | 91 | 95 | 90 | 87 | 63 | 75 | 75 |
| Inlet $SO_2$ (Dry), ppm | 2950 | 2500 | 2400 | 2250 | 2350 | 2150 | 1900 | 2100 | 2340 | 2200 | 2150 |
| Bed Temperature, °C | 415 | 400 | 350 | 390 | 390 | 415 | 425 | 440 | 465 | 455 | 455 |
| Sorbent Feed, kg/h | 668 | 1352 | 1111 | 1127 | 1177 | 311 | 375 | 412 | 488 | 839 | 859 |
| Available Cu, % | 2.5 | 2.8 | 2.8 | 2.9 | 3.1 | 7.0 | 5.2 | 4.4 | 2.9 | 3.0 | 3.0 |
| Cu/S Mole Ratio | 1.27 | 2.76 | 2.70 | 2.93 | 3.27 | 1.99 | 2.03 | 1.60 | 1.11 | 1.96 | 2.30 |
| Mole $SO_2$ Removed Per Moles Available Cu | 0.650 | 0.330 | 0.320 | 0.300 | 0.280 | 0.48 | 0.46 | 0.56 | 0.63 | 0.4 | 0.37 |
| Superficial Velocity, m/s | 0.98 | 1.13 | 0.91 | 1.04 | 0.94 | 1.10 | 1.16 | 1.19 | 1.25 | 1.31 | 1.16 |
| Bed Inventory, kg | 491 | 505 | 472 | 448 | 446 | 376 | 399 | 422 | 195 | 241 | 208 |
| Bed Depth, cm | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 46 | 46 | 46 |

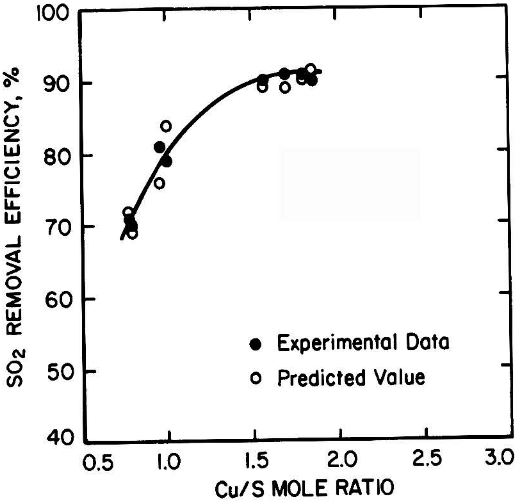


**Figure 5. Effect of available-copper to inlet-sulfur ratio on $SO_2$ removal efficiency (1.17-m bed).**

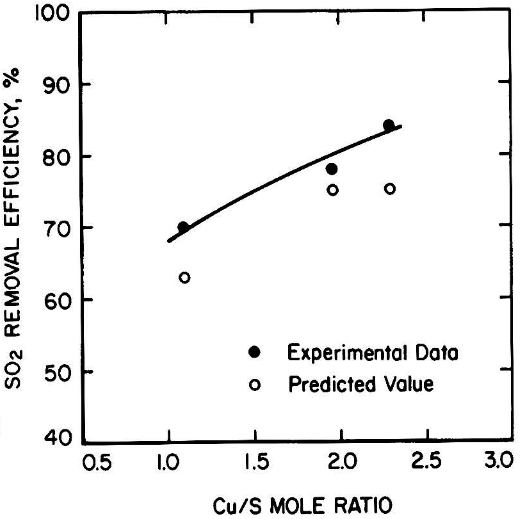


**Figure 7. Effect of available-copper to inlet-sulfur ratio on $SO_2$ removal efficiency (0.46-m bed).**

It must be pointed out that each test point has operating conditions different from those of the other test points because many of the predetermined test conditions were often not obtainable during the operating time available for each test point. Therefore, these test points are not expected to fall on a smooth curve. One might expect to see a smooth curve if only Cu/S mole ratio was changing while holding all other process variables constant. The curves shown in the figures were drawn only to show a trend as if Cu/S mole ratio were the only independent process variable. In fact, there are eight independent process variables. However, a nine dimensional plot is not possible to make. Both the experimental data and the model predictions are plotted in Figure 8 to evaluate the accuracy of the model. Most of the model predictions fall within a 5 percent deviation range. All reactor performance predictions for the 0.91-m expanded bed, and all but one of the reactor performance predictions for the 1.17-m expanded bed are within the 5 percent deviation range. However, for the 0.46-m expanded bed, two of the three reactor performance predictions fall outside of the 5 percent deviation range. In general, the model slightly underpredicts reactor performance and is therefore somewhat conservative.

In using the present reactor model to predict actual plant performance, it should be noted that the model is a function of seven variables. Errors in the measurement of any one of these variables during operation of the test unit would effect the model prediction. Some effects may be additive, while some may be compensative. In addition, the ideal flow model assumes the solid absorbent spheres are completely mixed in the reactor and that the reacting gas is not back-mixed (plug flow). These are only approximations; actual operation may only approach these conditions.

The reactor model predictions for the 0.46-m-deep bed are less successful than other test points. This could be due to a number of reasons, including errors in the measurements taken during operation. However, it is also possible that the assumptions on which the model is based, that is, a completely mixed sorbent and plug flow of the

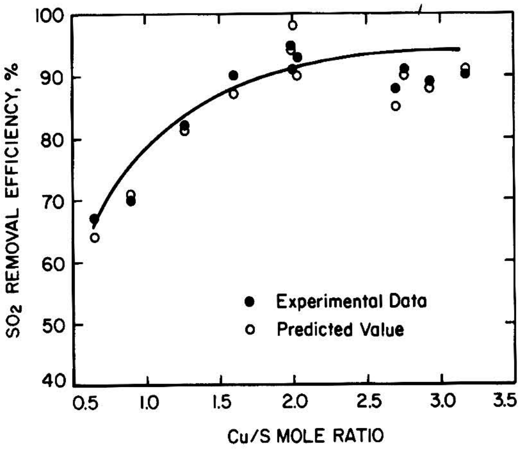


**Figure 6. Effect of available-copper to inlet-sulfur ratio on $SO_2$ removal efficiency (0.91-m bed).**

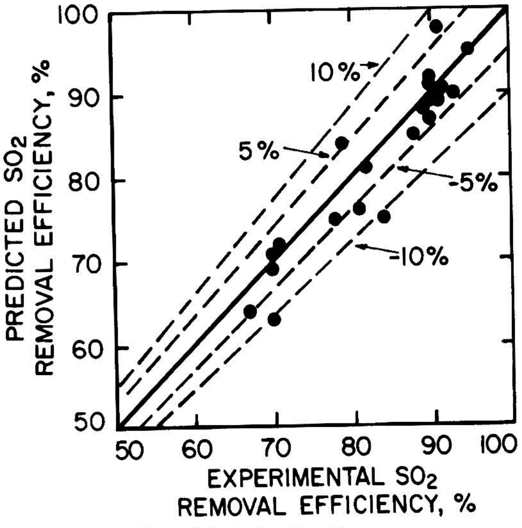


**Figure 8. Evaluation of model.**

flue gas, are not as valid for a shallow (0.46-m) bed. In particular, the sorbent feed port arrangement in the fluidized-bed reactor used in this study may have contributed to deviations from the assumed behavior of the reactor. The regenerated sorbent was fed near the distributor plate (near the bottom of the fluidized bed). This is suspected to cause some degree of accumulation of freshly regenerated sorbent feed immediately above the distributor plate. If this is true, then the solid particles in the fluidized bed are not ideally mixed. This would imply that more fresh feed with higher available copper content would be reacting with the incoming flue gas (with a high sulfur dioxide concentration) near the bottom of the fluidized bed. Because of the higher concentration gradients at the bottom reaction zone, higher sulfur dioxide removal efficiency could be obtained. This may partially account for the reactor model being slightly conservative overall. These differences may be more pronounced in the shallow bed because the shorter sorbent residence time of the shallow bed may result in increased stratification of the sorbent.

### Model Prediction

For process design purposes, the variables in the model were systematically varied to predict reactor performance under different operating conditions. The process variables studied are (1) sorbent copper content, (2) reactor bed depth, and (3) reaction temperature.

The effect of sorbent copper content on sulfur dioxide removal efficiencies was evaluated at different sorbent recirculation rates while keeping all other variables constant (See Figure 9). Three different levels of sorbent copper content were studied. The reaction rate constant (See Equation 11) has different values for different levels of sorbent copper content. The frequency factors in the reaction rate constant expression are 47,000, 34,130, and 19,871 ($h^{-1}$) for 5 percent, 7 percent, and 11 percent (by weight) copper, respectively. The study shows that sorbents with higher copper content require lower sorbent recirculation rates to reach the same level of sulfur dioxide removal. However, an excessive copper content in the sorbent may contribute to higher rates of sorbent attrition depending on the pore size of the alumina support used. One test was carried out in the microbalance reactor using sorbent containing 18 percent copper, and the sorbent support structure disintegrated after a few absorption-regeneration cycles even without any mechanical handling of the particles. The phenomenon was not observed using sorbents containing 11 percent or less copper. Experience obtained during the microbalance kinetics study indicates that 8 percent to 9 percent sorbent copper content may be an upper limit, although no quantitative data are available for an accurate assessment. Approximately 30 percent lower sorbent recirculation rates are required for a sorbent with 7 percent copper than for a sorbent with 5 percent copper (keeping other test conditions constant and maintaining a 90 percent sulfur dioxide removal efficiency).

The effect of bed depth on sulfur dioxide removal is presented in Figure 10. Four different bed depths were studied. At an expanded bed depth of 1.22 m, approximately 120 kg of sorbent is required to remove 90 percent sulfur dioxide from 1000 standard cubic meter of flue gas, while 150 kg of sorbent per 1000 standard cubic meter of flue gas is needed for a 0.91-m deep bed. The copper content of the sorbent was constant at 7 percent (by weight) in this analysis. However, deeper beds require more power to pull the flue gas through the fluidized bed. Economic optimization must be used to determine the most efficient design of the fluidized-bed absorber.

The effect of reaction temperature on sulfur dioxide removal is shown in Figure 11. As expected, higher reaction temperatures require less sorbent to achieve the same level of sulfur dioxide removal. At 455°C, the sorbent feed rate required for 90 percent sulfur dioxide removal is 25 percent lower than that required at 370°C. At 370°C, approximately 175 kg of sorbent is required to remove 90 percent of the sulfur dioxide from 1000 standard cubic meters of flue gas, while 130 kg of sorbent is needed at 455°C for 90 percent sulfur dioxide removal per 1000 standard cubic meters of flue gas.

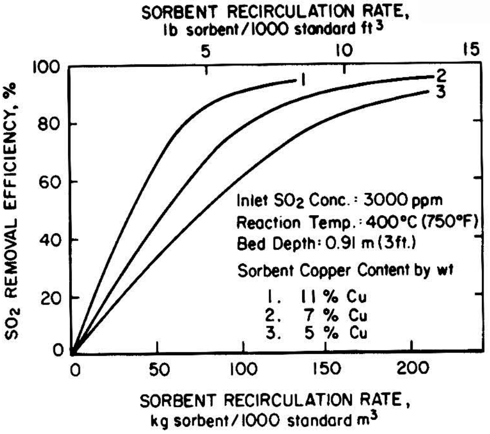


Figure 9. Effect of sorbent copper content on $SO_2$ removal.

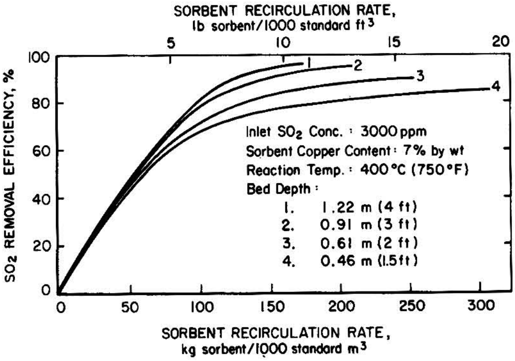


Figure 10. Effect of bed depth on $SO_2$ removal.

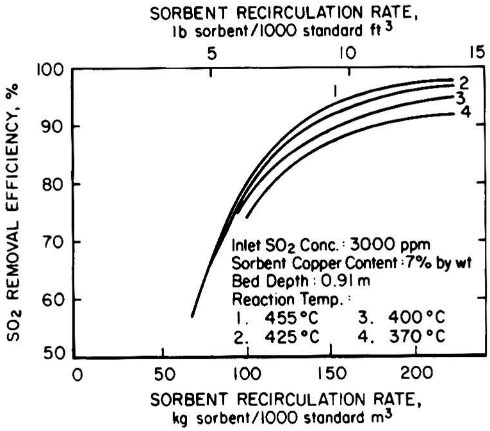


Figure 11. Effect of reaction temperature on $SO_2$ removal.

This reactor model was first provided to Science Management Corporation in 1983 [*13*] so they could make technical and economic evaluations, and optimize the design of the fluidized-bed copper oxide process.

### Comparison with Other Models

Recently, UOP, Inc., derived a semi-empirical regression model to describe fluidized-bed reactor performance using experimental data from the 1.02-m by 1.22-m fluidized-bed absorber at the Pittsburgh Energy Technology Center, [*4*] and the reaction rate equation developed by Yeh et al. [*11*]. The model described by McArdle et al. [*14*] was compared with experimental data with favorable results. The UOP, Inc., model uses a regressed coefficient in the rate constant equation. This establishes a least squares correlation between the regression model and the actual test data. This model is in good agreement with reactor performance over the range of operating conditions evaluated in the experimental program.

## CONCLUSION

The ideal flow reactor model developed here to describe the performance of the Fluidized-Bed Copper Oxide Process closely predicted the operation of an experimental apparatus. This steady-state model was slightly conservative in predicting sulfur dioxide removal efficiencies. The higher than average deviation in predicting the performance of a 0.46-m-deep bed was probably due to a combination of erroneous process measurements and nonideal mixing of solids. The model was formulated from basic physical laws, and because it has been validated by comparison with test data, enough confidence can be placed in the model to use it in the scale-up of the copper oxide process. The model can be used to predict reactor performance outside the test conditions conducted in the 1.02-m by 1.22-m fluidized-bed absorber. The next step in verification of this model would be a comparison with operation of a completely integrated process. After comparison with an integrated process, especially at lower expanded-bed heights, it could be determined whether any modifications to this model are required.

## DISCLAIMER

References in this paper to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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**James T. Yeh** received his B.S.Ch.E. degree at the National Cheng Kung University, Taiwan, China; M.S.Ch.E. degree at the University of Detroit; and Ph.D. degree at the Stevens Institute of Technology. He is currently a Chemical Engineer/Project Leader at the Pittsburgh Energy Technology Center, U.S. Department of Energy. His research interests include flue gas cleanup processes, coal combustion and MHD, fluidized-bed applications, reaction kinetics, and process simulation. He has worked for Princeton Aqua Science, Singer Simulation Products, and Procedyne Corporation.

**Charles J. Drummond** received his B.Ch.E. degree from Villanova University in 1973. His current position is that of Chief of the Solid Fuel Combustion Branch at the Pittsburgh Energy Technology Center of the U.S. Department of Energy. He is responsible for direction of the flue gas cleanup research conducted at the center. Mr. Drummond's research interests have also included the treatment of coal gasification and coal liquefaction process wastewaters.

**James I. Joubert** received his Ph.D. in Chemical Engineering from Worcester Polytechnic Institute in 1971. His current position is Director, Coal Utilization Technology Division, Pittsburgh Energy Technology Center, U.S. Department of Energy. His prior position in the DOE's predecessor agencies involved him in projects in the areas of combustion, flue gas cleanup, and magnetohydrodynamics.

# Chemistry of a Flue Gas Combined $NO_x$ and $SO_2$ Scrubber Employing Ferrous Cysteine Additives

**M. D. Tu and S. G. Chang**

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

*Use of ferrous cysteine additives in flue gas scrubbing systems creates a different and simpler scrubber chemistry compared to Japanese processes using ferrous chelates such as $Fe^{2+}$ (EDTA). Instead of being converted to nitrous oxide, nitric oxide in flue gas can be concentrated and/or reduced to nitrogen gas. Also, production of dithionate ions and nitrogen-sulfur compounds in scrubbing systems can be avoided. Fixation of nitric oxide occurs by a rapid reaction with the ferrous cysteine complex, at pH between 7.5 and 6.5, to form solid cystinatodinitrosyl iron (II), which releases NO upon heating. Most of the NO is reduced to gaseous species, primarily $N_2$, in ferrous cysteine solutions at pH 10. Cysteine can rapidly reduce ferric ion to ferrous ion while being oxidized to cystine. Cystine can be reduced back to cysteine by $SO_2$.*

## INTRODUCTION

The Japanese have developed several flue gas simultaneous desulfurization and denitrification processes in the 1970s, and have shown that these wet processes are very efficient in $SO_2$ and $NO_x$ removal (more than 85% for $NO_x$ and 95% for $SO_2$). However, these wet processes have not reached the commercial stage yet because they are uncompetitive economically, according to cost evaluations [*1*, 2].

The most promising type of wet process developed so far is based on the addition of ferrous chelates in scrubbing liquors to enhance the absorption of NO by forming nitrosyl ferrous chelates in aqueous solutions. The nitrosyl ferrous chelates can then react [*1*, *3*] with dissolved $SO_2$ and $O_2$ to produce $N_2$, $N_2O$, dithionate, sulfate and various N-S compounds [*1*, *4*, *6*] using the type of chelates patented by the Japanese, such as EDTA and NTA. Residual $O_2$ in the flue gas and intermediates produced in the system oxidize some of the ferrous chelates to ferric chelates, which are inactive. Therefore, this type of process requires regeneration of scrubbing liquors by removing dithionate, sulfate, and N-S compounds from the solutions and reduction of ferric chelates back to ferrous chelates.

The regeneration methods of scrubbing liquors and ferrous chelates associated with Japanese processes [2] are very costly. For example, in the Ashahi process, scrubbing liquors are pumped to an evaporator in the regeneration system. The concentrated solution from the evaporator is then pumped to a cooling crystallizer where hydrated sodium dithionate and sulfate crystals are produced under vacuum. These crystals are separated from the mother liquor in a screw decanter and sent to a dryer operating at 250°F-300°F, in which the hydrated crystals are converted to anhydrous sodium salts. Most of the mother liquor from the decanter is recycled to the reducing tank and a smaller stream is passed through a N-S compound treatment section. The N-S compounds are converted to relatively insoluble potassium salts by reaction with potassium sulfate. The potassium salts of the N-S compounds are separated in a screw decanter and sent to a thermal cracker for the decomposition at about 930°F.

The high capital investment cost of the Asahi process is due to the necessity for large absorbers, evaporators, crystallizers, dryers, rotary kiln crackers and screw decanter separators. The major operating and maintenance costs are electricity, fuel oil, steam and chemicals such as soda ash, EDTA and limestone. The requirement for consumption of large amount of energy is associated with the operation principle and design of the Asahi process.

We have recently developed new additives for combined removal of $SO_2$ and $NO_x$ from flue gas [*7*, *8*]. The new additives include ferrous cysteine, borate, and/or alkalis. Employment of these new additives creates a different and simpler scrubber chemistry compared to the Japanese processes using ferrous chelates such as $Fe^{2+}$ (EDTA). The production of dithionate and nitrogen-sulfur compounds can be suppressed or avoided by using these new additives. Ferric ions formed can be reduced by cysteine back to ferrous ions. This paper addresses the chemistry involving ferrous cysteine, NO, $SO_2$, and $O_2$ that applies to wet, flue gas clean up systems.

## EXPERIMENTAL SECTION

The reaction of ferrous cysteine with NO is influenced by the molar ratio of cysteine to ferrous ion, $n_{cysteine}/n_{Fe^{2+}}$, and the pH of the solutions. We have performed experiments to determine the absorption capacity of NO in aqueous solutions containing ferrous cysteine complexes at various $n_{cysteine}/n_{Fe^{2+}}$, pHs and at 55°C, using a bench-scale gas scrubber. Also, we have characterized the precipitates produced from reactions by means of an infrared spectroscopy and elemental analysis, and have analyzed the gaseous products by a mass spectrometry. Oxygen in flue gas

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M. D. Tu is on leave from Chemical Engineering Department, Chengdu University of Science and Technology, Chengdu, Sichuan, Peoples Republic of China can oxidize cysteine to cystine. This oxidation is catalyzed by ferrous ions. The effect of oxygen on the absorption of NO in ferrous cysteine solutions was also studied with the gas scrubber. $SO_2$ in flue gas can reduce cystine to cysteine. The reaction of $SO_2$ with cystine in solutions was characterized by laser Raman spectroscopy.

The general experimental procedure is outlined below for the case where $n_{cysteine}/n_{Fe^{2+}}$ in the reaction mixture is 4 and the reaction temperature is 55°C. 6.866 gm ($9 \times 10^{-2}$ M) $Na_2B_4O_7 \cdot 10H_2O$ (Baker reagent) as a buffer and 1.404 gm ($4 \times 10^{-2}$ M) cysteine · HCl · $H_2O$ (Baker reagent) were dissolved in 200 ml distilled water. The pH of the solution was adjusted to the desired value by addition of NaOH or $H_2SO_4$. The solution was transferred to a reaction column (50 mm ID × 210 mm, pyrex) and then purged with $N_2$ to remove $O_2$ from the system. 0.784 gm ($1 \times 10^{-2}$ M) $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Mallinckrodt reagent) was then added and the solution was again purged with $N_2$. The NO obtained from Matheson Co. was a mixture of 2.55% NO in $N_2$ with $NO_2$ impurity of less than 255 ppm; this mixture was further diluted to a NO concentration between 650 and 1000 ppm by adding $N_2$. The experiments were carried out by bubbling a mixture of NO and $N_2$ of known NO concentration through the ferrous cysteine solution, and the NO concentration in the outlet gas was measured with a Thermoelectron Model 14A chemiluminescent $NO_x$ analyzer. The gas flow rates were 630-800 mL/min. NO absorption was carried out until the NO concentration in the outlet gas became equal to that in the inlet gas, i.e., until saturation was reached. The resulting solutions were filtered in the absence of oxygen and the precipitates collected were dried in a vacuum dessicator. The precipitates were analyzed by infrared spectroscopy and elemental analysis.

Gaseous products were obtained when the reactions of NO with ferrous cysteine were carried out in a batch system at 25°C using a vacuum line set-up. 50 ml of distilled water was placed in a 100 ml round bottom flask and 0.702 gm ($8 \times 10^{-2}$ M) cysteine and 3.433 gm (0.18 M) $Na_2B_4O_7 \cdot 10H_2O$ (as buffer) were added. The pH of the solution was adjusted to the desired value by addition of NaOH or $H_2SO_4$. The flask containing the reaction mixture was evacuated and then filled with argon gas. 0.392 gm ($2 \times 10^{-2}$ M) $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ was added and the solution was again degassed. Pure NO (triple-distilled) was then expanded into the round bottom flask to about 760 mm Hg. The solution was stirred until the pressure over solutions stabilized, and a gas sample above the solution was allowed to expand into a previously evacuated flask for mass spectral analysis. The solution was then filtered, and the solid precipitate collected was dried and subjected to infrared studies and elemental analysis.

## RESULTS AND DISCUSSION

Figure 1 shows the effect of pH on the absorption of NO when the reaction temperature is 55°C and $n_{cysteine}/n_{Fe^{2+}}$ is 4. The amount of NO absorbed per mole of $Fe^{2+}$, $n_{NO}/n_{Fe^{2+}}$, and per mole of cysteine, $n_{NO}/n_{cysteine}$, increases from 0.5 to 2.7, and 0.12 to 0.70, respectively, as the pH of the solution increases from 6 to 8. The ratios $n_{NO}/n_{Fe^{2+}}$ and $n_{NO}/n_{cysteine}$ remain unchanged between pH 8 and 10. The effects of $n_{cysteine}/n_{Fe^{2+}}$ on $n_{NO}/n_{Fe^{2+}}$ and $n_{NO}/n_{cysteine}$ at pH 7 and 8 at 55°C are shown in Figure 2. The ratio $n_{NO}/n_{cysteine}$ decreases steadily from 0.57 to 0.24 as $n_{cysteine}/n_{Fe^{2+}}$ increases from 2 to 6 at pH 7. When the pH is 8, $n_{NO}/n_{cysteine}$ increases from 0.39 to 0.7 as $n_{cysteine}/n_{Fe^{2+}}$ increases from 2 to 4 and then gradually decreases to 0.64 at $n_{cysteine}/n_{Fe^{2+}}$ of 6. This same behavior was observed for $n_{NO}/n_{Fe^{2+}}$ in solutions at pH 7. The ratio $n_{NO}/n_{Fe^{2+}}$ reaches the maximum value of 1.5 at $n_{cysteine}/n_{Fe^{2+}}$ of 4 and decreases slightly with increasing $n_{cysteine}/n_{Fe^{2+}}$ ratio. However, at pH 8, $n_{NO}/n_{Fe^{2+}}$ increases monotonically from 0.78 to 3.82 as $n_{cysteine}/n_{Fe^{2+}}$ increases from 2 to 6.

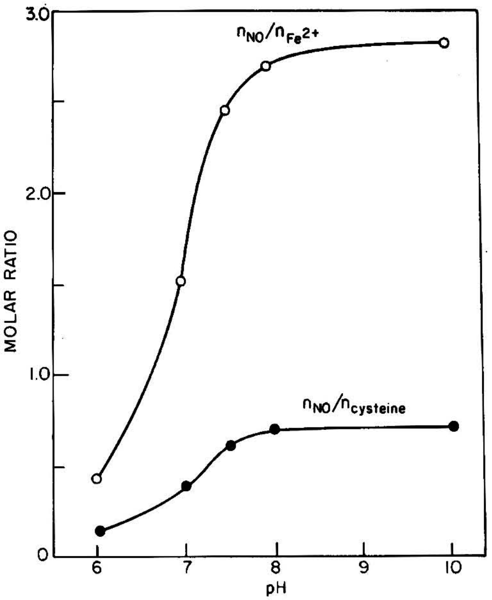

**Figure 1. The effect of pH on the absorption of NO in aqueous solutions containing ferrous cysteine at 55°C, with a molar ratio of cysteine to ferrous ion of 4.**

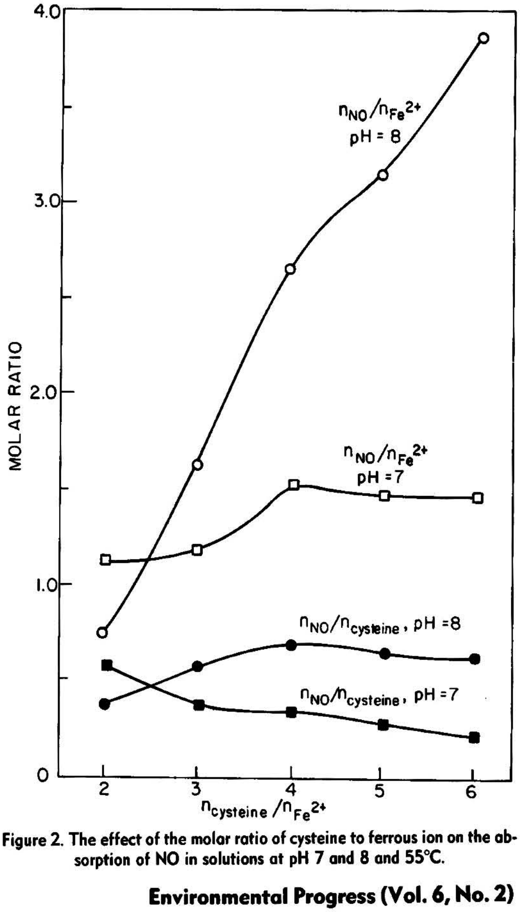

**Figure 2. The effect of the molar ratio of cysteine to ferrous ion on the absorption of NO in solutions at pH 7 and 8 and 55°C.**

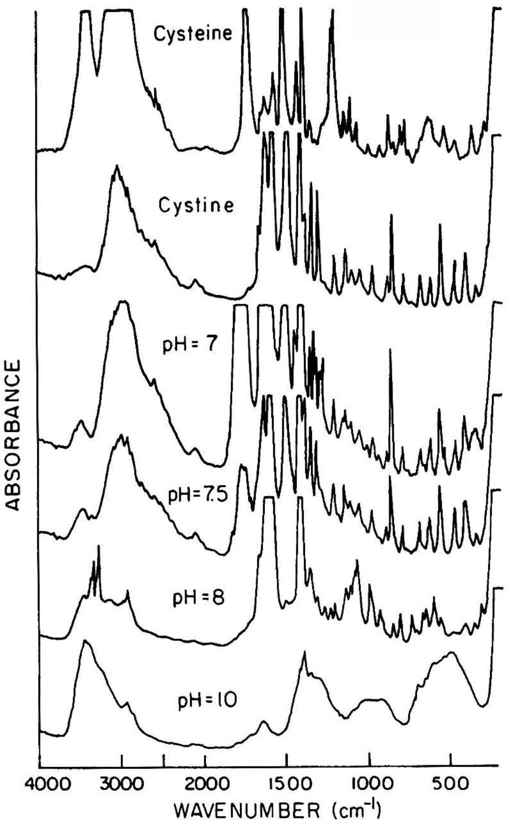

**Figure 3. Infrared spectra of cysteine, cystine, and solid products of the reaction $Fe^{2+}$ + 4 cysteine + NO at different pHs and 55°C.**

Varying the pH of the solution and the ratio of cysteine to $Fe^{2+}$ not only affects the amount of NO absorbed but also changes the nature of the reaction products. Figure 3 shows the IR spectra of the precipitates obtained from the reaction of ferrous cysteine ($n_{cysteine}/n_{Fe^{2+}} = 4$) with NO at 55°C and different pH's. Also shown in Figure 3 are the IR spectra of solid cysteine and cystine for comparison. It is obvious from these IR results that the nature of the solid is very different when the pH of solutions is changed from 7 to 10. The IR spectra of precipitates at pH 7 show several bands at 350(sh), 515(m), 920(w), 990(w), 1140(sh), 1255(m), 1265(m), 1310(m), 1430(m), and 1775(s) $cm^{-1}$, in addition to all the bands of cystine (where s, m, w, and sh indicate strong, medium weak, and shoulder respectively). The band at 1775 $cm^{-1}$ can be attributed to the M-NO stretching $\nu_{M\text{-}NO}$. The relative intensity of this band decreases in spectra of precipitates obtained at pH 7.5, where the only other bands observed are those of cystine. The IR spectra of solids at pH 8 show different features than those at pH 7 and 7.5. The 1775 $cm^{-1}$ $\nu_{M\text{-}NO}$ band disappears, as do those bands due to cystine as observed in solids obtained at pH 7 and 7.5. However, the absence of the cystine bending bands $\delta_s\text{-}NH_3^+$ (1490 $cm^{-1}$), $\delta_{as}\text{-}NH_3^+$ (1580 and 1620 $cm^{-1}$), the stretching band $\nu_{\text{-}NH_3}{}^+$ (3030 $cm^{-1}$); and the presence of $\nu_s\text{-}NH_2$ (3280 $cm^{-1}$), $\nu_{as}\text{-}NH_2$ (3350 and 3370 $cm^{-1}$) indicate the bonding of the cystine amino group to the ferrous ion. The IR spectra of solids at pH 10 resemble those of $Fe(OH)_2$ and/or $Fe(OH)_3$. The complete assignment of IR bands are in progress. The IR results are in good agreement with the results of elemental analysis. Table 1 shows the $n_{NO}/n_{Fe^{2+}}$ and $n_{cysteine}/n_{Fe^{2+}}$, obtained from elemental analysis, for the precipitates of the reactions at pH 7 and 8 and 55°C. The solids at pH 7 contain two moles of NO per mole of $Fe^{2+}$ found (Table 2), whereas the solids at pH 8 do not contain any NO. The solids obtained from reactions at pH 10 and 55°C contain iron, but neither cysteine nor NO.

The influence of $n_{cysteine}/n_{Fe^{2+}}$ on the nature of precipitates produced was studied. Figure 4 shows the IR spectra of solids obtained at pH 7 and 55°C. A strong band at 1775 $cm^{-1}$ was observed for all ratios of $n_{cysteine}/n_{Fe^{2+}}$. Additional bands at 515, 990, 1255, 1265, 1310, and 1430 $cm^{-1}$ appear in spectra of solids obtained when the ratio of $n_{cysteine}/n_{Fe^{2+}}$ is more than 3. Figure 5 shows IR spectra of the precipitates collected from the reaction at pH 8 and 55°C. There is no NO complex in the reaction products as is evident

TABLE 1. THE CHEMICAL COMPOSITION OF PRECIPITATES FROM AQUEOUS REACTIONS OF FERROUS CYSTEINE, AT SEVERAL MOLAR RATIOS OF CYSTEINE TO FERROUS ION, WITH NO AT pH 7 AND 8, AND 55°C

| | $(n_{cysteine}/n_{Fe^{2+}})$ solution | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| pH 7 | $\left(\frac{n_{NO}}{n_{Fe^{2+}}}\right)$ ppt | 1.95 | 1.9 | 2.2 | 2.1 | 1.92 |
| | $\left(\frac{n_{cysteine}}{n_{Fe^{2+}}}\right)$ ppt | 3.0 | 2.0 | 2.0 | 4.3 | 2.0 |
| pH 8 | $\left(\frac{n_{NO}}{n_{Fe^{2+}}}\right)$ ppt | 0 | 0 | 0 | 0 | 0 |
| | $\left(\frac{n_{cysteine}}{n_{Fe^{2+}}}\right)$ ppt | 1.73 | 2.07 | 2.14 | 2.83 | 3.42 |

TABLE 2. THE ELEMENTAL ANALYSES OF PRECIPITATES FROM REACTIONS OF FERROUS CYSTEINE WITH NO AT pH 7 AND 55°C

| $n_{cysteine}/n_{Fe^{2+}}$ | C (%) | H (%) | N (%) | S (%) | Fe (%) | Empirical Formula |
|---|---|---|---|---|---|---|
| 2 | 20.27 | 3.80 | 11.90 | 16.69 | 9.59 | $Fe(C_3H_7NS)_3(NO)_2$ |
| 3 | 19.66 | 3.40 | 14.85 | 17.73 | 14.70 | $Fe(C_3H_6NS)_2(NO)_2$ |
| 4 | 20.88 | 3.60 | 14.83 | 17.82 | 13.10 | $Fe(C_3H_6NS)_2(NO)_2$ |
| 5 | 24.26 | 4.18 | 13.48 | 20.56 | 8.65 | $Fe(C_3H_7NS)_4(NO)_2$ |
| 6 | 19.67 | 3.58 | 14.15 | 17.10 | 14.12 | $Fe(C_2H_7NS)_2(NO)_2$ |

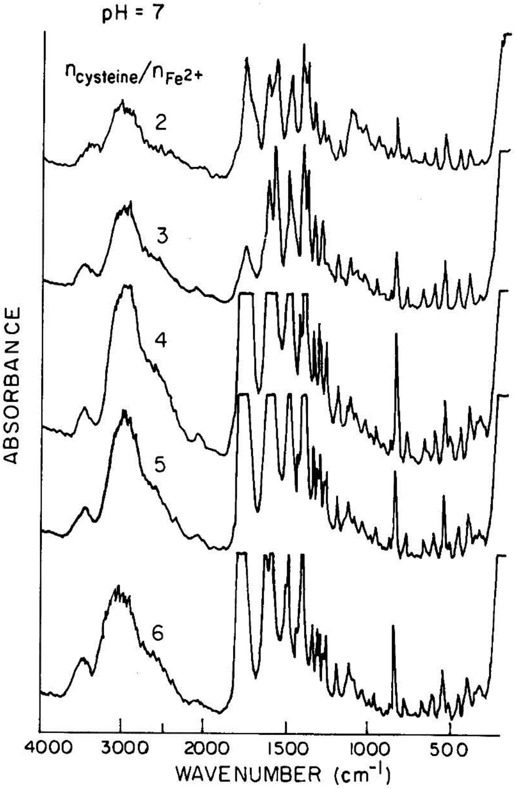

**Figure 4.** Infrared spectra of solid products from reactions of NO with ferrous cysteine at various molar ratios of cysteine to ferrous ion and at pH 7 and 55°C.

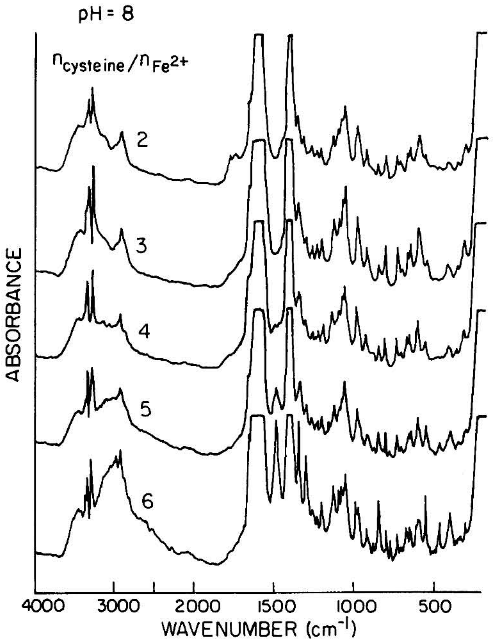

**Figure 5.** Infrared spectra of solid products from reactions of NO with ferrous cysteine at various molar ratios of cysteine to ferrous ion and at pH 8 and 55°C.

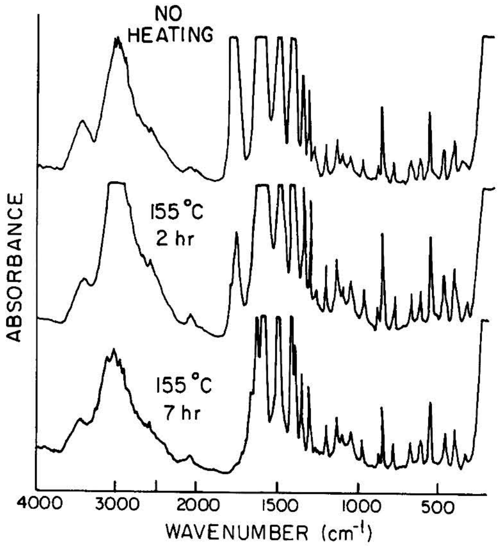

**Figure 6.** Infrared spectra showing the thermal stability (at 155°C) of solid products obtained from reaction $Fe^{2+}$ + 4 cysteine + NO at pH 7 and 55°C.

from the absence of any band at 1775 cm$^{-1}$. Notice the increase in the intensity of the bands at 550, 849, 1125, 1300 and 1340 cm$^{-1}$ as the $n_{cysteine}/n_{Fe^{2+}}$ increases from 2 to 6. Additional bands at 775 and 1470 cm$^{-1}$ were observed for solids obtained when the ratios of $n_{cysteine}/n_{Fe^{2+}}$ were 4, 5 and 6. Two more bands were observed at 455 and 870 cm$^{-1}$ when the ratio was 5 or 6.

When the solid sample containing M-NO was subjected to heating (~155°C) or vacuum ($\leq 10^{-2}$ torr), NO was released. Figure 6 shows the IR spectra of solids after heating at 155°C for 2 and 7 hours. Part of the NO was released after heating the solid sample for 2 hrs, and all the NO had disappeared after heating for 7 hrs. Analysis of the gaseous species evolved after heating showed mostly NO with a trace of $N_2O$. This again confirms that absorbed NO is present in the solid precipitates.

The analyses of gaseous products from the reaction of ferrous cysteine with NO by mass spectrometry indicate that, at pH 10, all the NO absorbed is reduced by the ferrous cysteine to yield a mixture of $N_2$ (78.5%) and $N_2O$ (21.5%). At pH 8, 46.5% of the absorbed NO is converted to a mixture of $N_2$ (54.0%) and $N_2O$ (46.0%), while the rest remained in solution (none was found in the precipitates, as can be seen in Table 1). At pH 7, 45.7% of the absorbed NO is reduced to a mixture of $N_2$ (46.7%) and $N_2O$ (50.3%). The rest of the absorbed NO presumably ends up in the precipitates (Figure 4 and Tables 1 and 2) and possibly some remaining in solution.

The reactions of NO with ferrous cysteine in solution are affected by the concentration of reactants and pH of the solutions. The reactions involved have not been well characterized. However, the following reaction sequence appears to take place,

$$Fe^{2+} \xrightarrow{+CyS^-} Fe(CyS)_2 \xrightarrow[-N_2\uparrow\ -\ N_2O\uparrow]{+NO} Fe(CySSCy)(NO)_2\downarrow$$

$$\xrightarrow[\Delta]{-NO\uparrow} Fe(CySSCy) \xrightarrow{+CyS^-} Fe(CyS)_2 + CySSCy$$

where CyS and CySSCy are cysteine and cystine, respectively.

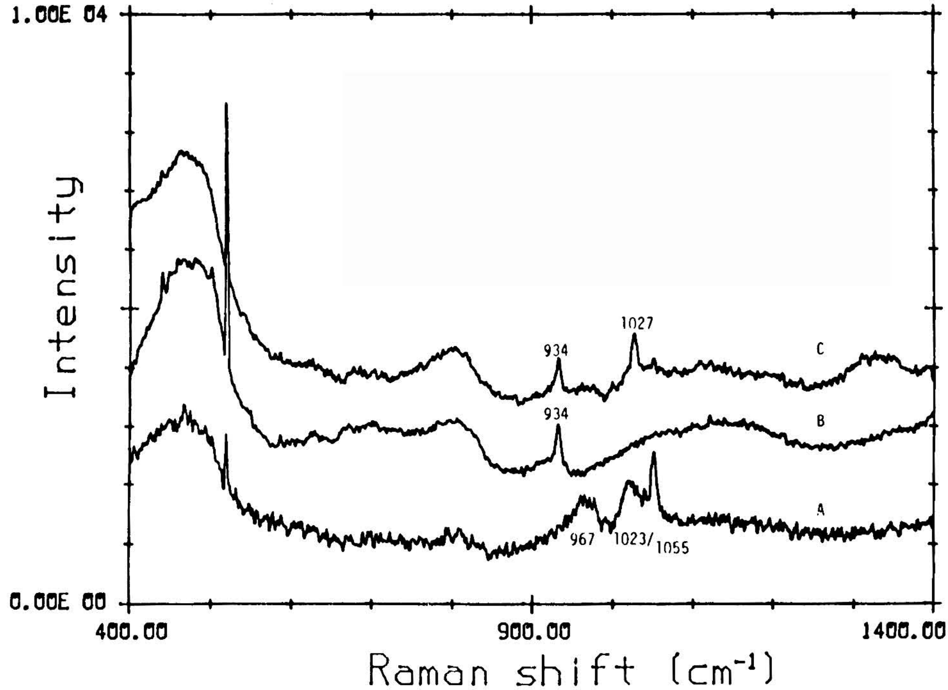

**Figure 7. Raman spectra of a mixture of (A) $HSO_3^-/SO_3^{2-}$ at pH 7; (B) cystine/$ClO_4^-$; and (C) $HSO_3^-/SO_3^-$ with cystine/$ClO_4^-$ at pH 7.**

Oxygen, at a concentration of about 5% in flue gas, can dissolve in ferrous cysteine solutions and oxidize the ferrous ion to ferric ion, and thus decrease NO absorption efficiency. An experiment was carried out by bubbling a mixture of gases, composed of 800 ppm NO and 5% $O_2$ in $N_2$, into a $10^{-2}$ M ferrous cysteine solution ($n_{cysteine}/n_{Fe^{2+}} = 1$). The result shows a substantial 92.8% reduction in NO absorption, compared to the case where there was no oxygen in the flue gas (Table 3). A separate run was conducted for solutions containing $Fe^{2+}$ (EDTA) under similar conditions to those used for $Fe^{2+}$ (cysteine). The results indicated a 90% reduction in NO absorption with the presence of 5% $O_2$. The NO absorption capacity of $Fe^{2+}$ (cysteine) solutions is almost twice as much as that of $Fe^{2+}$(EDTA) solutions in the absence of $O_2$, and about 30% more with 5% $O_2$, under experimental conditions employed (Table 3).

Once ferrous ion is oxidized to ferric ion by $O_2$, cysteine can rapidly reduce ferric ion back to ferrous ion while being oxidized to cystine. Reactions of $O_2$ with ferrous cysteine in solution can be represented by

$$Fe^{2+}(CyS^-)_2 \xrightarrow{O_2} Fe^{3+}(CyS^-)_2 \rightarrow Fe^{2+}(CySSCy) \xrightarrow{CyS^-} Fe(CyS)_2 + CySSCy$$

TABLE 3. COMPARISON OF NO ABSORPTION CAPACITY IN AQUEOUS SOLUTIONS CONTAINING $Fe^{2+}$(CYSTEINE) AND $Fe^{2+}$(EDTA)

($Fe^{2+}$ = cysteine = EDTA = $10^{-2}$ M, $P_{NO}$ = 800 ppm, pH = 7 and at 55°C)

| Metal Complexes | $O_2$ | NO absorbed (M) |
|---|---|---|
| $Fe^{2+}$(cysteine) | 0 | $9.0 \times 10^{-3}$ |
| | 5% | $6.5 \times 10^{-4}$ |
| $Fe^{2+}$(EDTA) | 0 | $5.0 \times 10^{-3}$ |
| | 5% | $5.1 \times 10^{-4}$ |

Sulfite and bisulfite ions do not appear to react with coordinated NO in ferrous nitrosyl cysteine complexes. However, they do react with cystine to form cysteine and thiocysteine, as shown in Figure 7. The Raman shifts at 934, 967, and 1023/1055 cm$^{-1}$ correspond to $ClO_4^-$, $SO_3^{2-}$, and $HSO_3^-$ respectively, where $ClO_4^-$ was used as a reference compound. A new Raman peak at 1027 cm$^{-1}$ appears after mixing the $SO_3^{2-}/HSO_3^-$ with cystine/$ClO_4^-$ solutions. The 1027 cm$^{-1}$ peak corresponds to thiocysteine. The Raman shifts for cysteine and cystine are too weak to be detected at the concentrations employed. The equilibrium constants of the reactions have been determined at various pHs.[9]

Thiocysteine can undergo hydrolysis to produce cysteine and sulfate. The hydrolysis rate is acid catalyzed and is very slow unless at very low pH conditions. Reactions of $SO_2$ with cystine in solutions can be shown as follows:

$$CySSCy \xrightarrow{HSO_3^-} CyS^- + CySSO_3^- \xrightarrow{H^+} CyS^- + HSO_4^-$$

## CONCLUSION

The cysteine can bind to ferrous ion to form ferrous cysteine, which can efficiently bind and react with NO to form cystinatodinitrosyl iron(II), $Fe(CySSCy)(NO)_2$. When ferrous ion is oxidized to ferric ion by residual oxygen in flue gas, cysteine can reduce ferric ion back to ferrous ion very quickly, while cysteine is reduced to cystine (a dimer of cysteine). Both cystine and cystinatodinitrosyl iron(II) are not very soluble in neutral aqueous solutions, and will precipitate. Cystinatodinitrosyl iron(II) can undergo thermodecomposition at a relatively low temperature (T ~

150°C) to produce ferrous cystine and release NO. The concentrated NO gas can be recycled into the boiler or used for $HNO_3$ manufacturing. The ferrous salts can be recycled. The cystine can dissolve in basic solutions and be reduced to cysteine for recycling by either chemical or electrochemical reduction methods, which are commercially available techniques. Also, the cystine can be reduced by absorbed $SO_2$ (sulfite/bisulfite) to produce cysteine and cysteinesulfonate, which will undergo acid-catalyzed hydrolysis to form cysteine and sulfate.

In the Japanese processes, dithionate ion is produced as a result of the reduction of ferric ion by bisulfite, and N-S compounds are produced[1] as a result of reaction between $Fe^{2+}$(EDTA)NO and bisulfite/sulfite. In processes using ferrous cysteine additives, ferric ion can be reduced by cysteine rapidly, therefore minimizing the possibility of ferric ion interacting with bisulfite, and dithionate formation can be minimized or eliminated as a result. Also, the coordinated NO in cystinatodinitrosyl iron(II) does not appear to react with dissolved $SO_2$ to produce N-S compounds.

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**M. D. Tu** graduated from the Post Graduate School of Chengdu Polytechnical Institute, Sichuan, People's Republic of China. She was a visiting scholar at Tufts University, Massachusetts, and at Lawrence Berkeley Laboratory, University of California in 1984 and 1985. She is currently a professor at the Department of Chemical Engineering, Chengdu University of Science and Technology.

**S. G. Chang** obtained a B.S. degree in Chemical Engineering from National Taiwan Cheng-Kung University, and a Ph.D. degree in Chemistry from University of California at Berkeley. He is a principal investigator of the Flue Gas Scrubber Chemistry Project in the Applied Science Division of Lawrence Berkeley Laboratory, University of California. The field of his interest is environmental chemistry including atmospheric chemical transformation and air pollution control studies. He has published more than fifty scientific papers and reports.

# The Hazardous Waste Research Center at Louisiana State University

**Rosalind Segesta and Louis J. Thibodeaux**

3418 CEBA, Hazardous Waste Research Center
Louisiana State University
Baton Rouge, LA 70803

*Hazardous waste and the problems associated with its proper disposal are the concerns of the Hazardous Waste Research Center (HWRC), located on the Baton Rouge Campus of Louisiana State University.*

*The Center is a part of the U.S. Environmental Protection Agency's "Centers of Excellence" program to conduct long-term fundamental research in 3 major areas:*
*(1) incineration/combustion;*
*(2) alternate methods of treatment/destruction;*
*(3) chemicals/materials interaction and stabilization.*

*The projects are interdisciplinary in scope, with faculty members from civil, mechanical, and chemical engineering, chemistry, and the marine sciences participating.*

*Future research directions will change to keep pace with the problems and needs of industry, waste handlers, government, and the public. The Hazardous Waste Research Center, in dealing with current problems and anticipating future needs, will help reduce the risk and/or extent of negative impact on the environment, on human health, or on the economy of the nation due to improper management or disposal of hazardous wastes.*

## INTRODUCTION

In September, 1981 Louisiana State University in Baton Rouge was selected from a group of 27 competing universities in the United States to house the Hazardous Waste Research Center (HWRC). The Center was established as a part of the U.S. Environmental Protection Agency's Centers of Excellence program, created as a result of the passage of the Research and Development Act of 1978, and administered through the Office of Research and Development (ORD, Washington). This particular piece of legislation contained a Congressional request for examination of alternative approaches for conducting long-term environmental research within EPA. In response, in April, 1978, EPA published a report to the President entitled "Laboratories Needed to Support Long-term Research in EPA." Subsequent Congressional action provided funds for establishing the institutional Centers. The Center at LSU is one of eight such centers, and was the last to be established (three in 1979, four in 1980, and the HWRC in 1981). The mission of the Centers of Excellence program is long-term, fundamental research on selected environmental topics. The eight centers are as follows:

| | | |
|---|---|---|
| (1) | Groundwater Research Center | University of Oklahoma<br>Oklahoma State University<br>Rice University |
| (2) | Pollution Human Health Effects Research Center | University of Pittsburgh |
| (3) | Marine Sciences Research Center | University of Rhode Island |
| (4) | Pollutant Intermedia Transport Research Center | University of California/L.A. |
| (5) | Ecosystems Research Center | Cornell University |
| (6) | Advanced Environmental Control Technology Research Center (municipal wastes) | University of Illinois |
| (7) | Industrial Waste Elimination Research Center | Illinois Institute of Technology<br>University of Notre Dame |
| (8) | Hazardous Waste Research Center | Louisiana State University |

Certain legislation was fundamental in laying the groundwork for research in the area of hazardous waste treatment/disposal. The first far reaching legislation addressing the hazardous waste problem was the Resource Conservation and Recovery Act (RCRA), passed by Congress in 1976. Prior to this time, hazardous waste had been controlled primarily by state or local governments. In many cases, the states were doing an adequate job but, in others the results proved to be far from satisfactory. Since there was no regulatory meaning to the term hazardous waste, waste management was usually equated with land disposal or discharge into bodies of water. However, as these wastes tended to migrate into environmentally sensitive areas, it became apparent that land disposal was not an adequate long-term solution for many of the hazardous waste problems generated by a technological society such as ours. The problem of waste disposal became a national concern in the mid- to late 1970s as it became increasingly evident at many waste sites that mismanagement and indiscriminate dumping were causing harmful substances to be released into the land, the water, and the air. Publicity received in incidents such as the Love Canal in New York and the PCB contamination in Michigan has increased public awareness about the effects of improper disposal of hazardous waste on health and the environment. It was also becoming increasingly clear that even well-intentioned and long-accepted waste management practices, particularly the use of landfills, surfaces impoundments, and lagoons, might constitute substantial threats, arising from the potential slow leakage of waste constituents or leachate through the soil and into the ground water (which constitutes the primary source of drinking water for many communities).

RCRA, as passed, covered several different aspects of the management of hazardous waste. In December, 1978, EPA under the auspices of RCRA, proposed regulations for the generation, transport, and disposal of hazardous waste. In May 1980 many of the proposed regulations were put into final form, and went into effect on November 19, 1980. This is the so-called cradle-to-grave approach, since proposed regulations governed the generation, transportation, and disposal/treatment of hazardous waste, the intent being to regulate hazardous wastes produced in the future. The treatment and disposal portion of the regulations provided only guidance for interim-status facilities (i.e., those in place as of November 19).

In 1981, as the second phase of the program, EPA issued regulations for new facilities. The problem inherent in such an approach was that previously abandoned disposal sites with uncontrolled releases of waste into the environment were not effectively addressed by RCRA, which was primarily concerned with the proper management of present and future hazardous waste. Because of the many problems posed by uncontrolled hazardous waste sites, both active and inactive (particularly those abandoned sites whose ownership was unknown), Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), which later became known as Superfund. Problems associated with the identification of especially threatening uncontrolled hazardous waste sites became prominent, including locating such sites, characterizing their contents, detecting the nature and extent of releases into the environment, substantiating actual or potential adverse impacts on health and the environment, and developing cleanup techniques and plans.

RCRA has had a major effect on the way in which the chemical industry treats and disposes of its wastes. The regulations promulgated have both favored certain types of treatment and disposal and provided the economic incentive to modify manufacturing processes so as to minimize the production of residuals that must be discarded. Such improved management of hazardous waste, of course, implies greater costs to industry and eventually to the public, either directly or indirectly. The alternative, however, would lead to even greater costs in the future and to unacceptable effects on human health and the environment. And when one considers that approximately 255 million to 275 million metric tons of hazardous waste under Federal and state regulations are generated annually, and that it is estimated that by 1990, more than $12 billion (in 1981 dollars) will be required to manage regulated wastes, the need for more efficient waste technologies becomes apparent.

Hazardous waste problems, then, are an integral element of life as we know it. The non-existence of such problems goes hand-in-hand with the non-existence of the chemical process industry (CPI), the automobile industry, etc.. If we continue to produce goods that have a chemical basis in production or refinement, we will continue to produce hazardous chemical wastes. Because of the growing trend in the CPI toward the production of relatively small quantities of specialty chemicals, a potpourri of hazardous waste treatment/disposal processes will be needed to handle the varied wastes from these operations. The imminent bloom of the bio-technology and synthetic fuel industries will demand additional diversification in these areas.

A key feature of any program dealing with hazardous waste and the conversion of identifiable chemical species to environmentally compatible chemical species, then, will be the development of a number of alternative approaches and processes. Figure 1 illustrates what the HWRC feels represents a general conceptual approach to the treatment and disposal of hazardous waste, an approach involving long-range exploratory research in the areas of conversion, separation, and media interaction. This hierarchial approach has an inherent chemical process nature, which is entirely appropriate, since hazardous wastes consist of identifiable chemical substances.

Concomitant research is needed in each of these areas, so that a holistic approach is pursued. Long-term research efforts aimed only at conversion (i.e., destruction) without regard to the problems of separation (i.e., extraction) or some preparation process would be short-sighted. Research into traditional or new chemical/physical separation processes without proper regard to the air, water, and soil/waste mixture interactions would also be very short-sighted because of the intimate involvement of these natural media and hazardous wastes.

The Hazardous Waste Research Center, located in the center of the lower Mississippi River industrial corridor, affords an excellent location for research in the areas of hazardous waste treatment and disposal. The Center consists of three fundamental program areas: (1) basic research; (2) applied research; and (3) technology transfer. The basic research program, the Center's primary focus, can be divided into three areas: (1) incineration/combus-

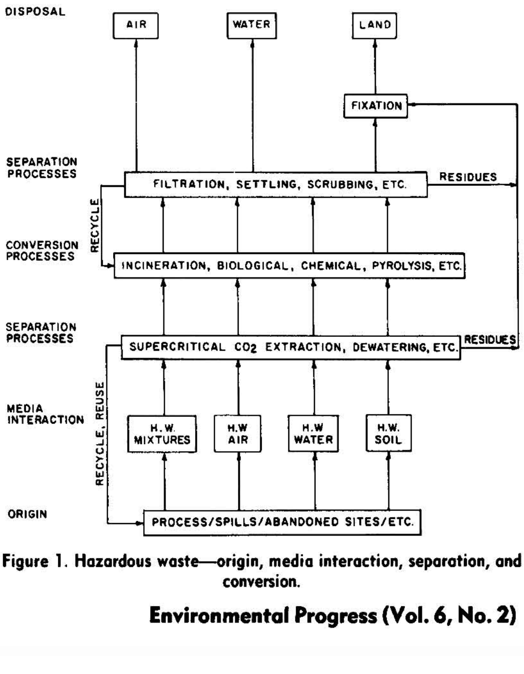


**Figure 1. Hazardous waste—origin, media interaction, separation, and conversion.**

tion; (2) alternate methods of treatment/destruction; and (3) chemicals/materials interaction and stabilization. Prior to the establishment of the HWRC, waste treatment/disposal was handled in a number of ways. It was with these available technologies in mind, along with the knowledge of the problems resulting from certain of these, that the three areas of basic research were selected. The Center's projects are interdisciplinary in scope, with faculty members from chemical, civil, and mechanical engineering, chemistry, and the marine sciences participating at present. Future directions can and probably will change to keep pace with the changing problems and needs of industry, waste handlers, the government, and the public.

In addition to the basic research program, two adjunct programs currently exist, an applied research program and a technology transfer program. The applied research program focuses on the establishment of a working relationship with industry so as to define and serve their immediate needs. This area of endeavor has not been extremely active in the past, but strides are currently being made to develop this program so that a truly working relationship between local industry and the Center exists. The objective of the second adjunct program, the technology transfer program, is to communicate results generated from HWRC projects to industry, government agencies, academia, and the public.

The Center's organizational structure is as follows. At the apex of the structure is the U.S. EPA Office of Research and Development (ORD) Centers Council, comprised of senior ORD officials in addition to one representative of the scientific community acquainted with the Center's program and a member of the Center's Scientific Advisory Committee (SAC). Its primary responsibilities are: (1) to recommend basic policies and procedures for operation of the Centers Program as a whole; (2) to recommend procedures for periodic review of the Centers and to assist in the development of review criteria; and (3) to review recommendations regarding funding levels for the Centers Program. Robert A. Papetti is Director of the Centers Program for ORD.

Next in the line of management is the EPA project officer, Clyde Dial (HWERL) who represents EPA's primary liaison with the Center and provides administrative guidance. In addition, he provides overall guidance for the projects and assists the Director in preparing funding recommendations for Center projects.

There are also two Center Advisory Committees. The first is the Scientific Advisory Committee (SAC), composed of nationally known scientists and researchers from industry, academia, and the EPA. The committee's chief function is to provide advice and consultation to the Center's Director and researchers on the merit of proposed and ongoing work in the basic research program. Committee members are available to consult with individual researchers as necessary. The second committee, the Industrial Advisory Committee, composed of local industry representatives, was organized to contribute to the applied research program by assisting in the industry needs identification process, and by making recommendations as to the best approaches to pursue in solving the identified problems.

The core staff is responsible for the overall functioning of the HWRC program. The Director oversees the day-to-day operations in accordance with general guidelines set forth by the Centers Council through the EPA project officer. He also serves as the liaison between the Center researchers and the project officer. The staff assistant coordinates daily administrative operations including budgeting, personnel supervision, information requests, and numerous public relations activities. The technology transfer group coordinates media activities for the Center, including organizing seminars and symposia to convey technical information, and maintaining an information center for the public. The Quality Assurance Officer's primary responsibility is to ensure that all environmentally related measurements result in data of known quality, and to serve as a liaison between EPA's Quality Assurance Management Staff (QAMS) and Center researchers.

As alluded to earlier, hazardous waste management has evolved to a central issue in the overall environmental policy in most industrialized nations. This development reflects the growing awareness that in no other field of environmental protection is one faced at the same time with such high quantities and concentrations of solid, liquid, and gaseous hazardous pollutants. Moreover, the problem is a permanent one, both from the point of view of generation and disposal, and must be addressed immediately. The projects sponsored by the HWRC are designed to investigate various treatment/disposal technologies.

Presently, seven projects are being funded through the Center, three in the area of incineration, two in alternate methods of treatment/destruction, and two in chemicals/materials interaction and stabilization. A brief discussion of each project follows.

The first of the incineration projects is entitled "Destructibility of Pure Hazardous Waste Compounds in a Laboratory Flame Environment." The principal investigators are Vic Cundy and Tom Lester. The goal of this research effort is to determine the basic combustion kinetics in a laboratory flame environment using a flat flame burner. The specific objectives of this study include the following:

1) To design and fabricate a laboratory scale, flat flame burner facility. This phase of the project has been completed, resulting in the development of the flat flame burner, its housing, microprobes for gas sampling, and thermocouple probes for temperature measurement.
2) To test the developed flat flame facility and demonstrate the validity of the measurement techniques.
3) To obtain both stable specie concentration profiles and temperature profiles from flames generated in the flat flame facility. Flames being studied contain various amounts of chloromethane, dichloromethane, chloroform, or carbon tetrachloride seeded with methane. Air or oxygen is used as the oxidizing agent.
4) To determine the net reaction rate for desired stable species from quasi one-dimensional flame equations, stable specie profiles, and temperature measurements. Diffusional and bulk velocity effects will be used to determine the net reaction rate for each desired stable species.
5) To determine reaction rate constants for binary and multicomponent reactions from corresponding net reaction rates.

To date, chloromethane and dichloromethane have been studied, and global kinetic models are being developed to predict their incinerability characteristics. Analytical studies (primarily gas chromatography using FID, ECD, and TCD, and more recently GC/MS) have indicated the presence of many stable intermediates (PICs) close to the burner. Certain of these compounds are equally, if not more hazardous than the compounds being studied.

The second incineration project is entitled "Incineration of Liquid Hazardous Waste Droplets." The principal investigators are Arthur Sterling, Ed K. Hurt, and Ailene G. Gardner. This project focuses on the atomization of liquid wastes. A study of the spray combustion phenomenon will integrate the effects of droplet-droplet interaction experiments with single droplet experiments through development of a well-controlled physical simulation of the spray combustion process. It is the goal of this study to improve the mathematical models for spray combustion of hazardous liquid wastes, since some degree of droplet-droplet interaction will be taken into account. The specific objectives of this study are as follows:

1) To develop an experimental facility to observe, measure, and characterize the transient behavior of hazardous waste droplets in a well-controlled flame environment, taking into account droplet-droplet interactions.
2) To provide a ranking of incinerability of liquid hazardous wastes as pure compounds and mixtures based on the experimental design.
3) To identify liquid phase reaction products that would affect the destruction and removal efficiency (DRE) of liquid hazardous waste.

The third and final incineration project is entitled "Combustion Characteristics of Selected Chlorinated Hydrocarbons." The principal investigator is Richard Matula. The ultimate goal of this effort is the development of an understanding of the combustion characteristics of a selected group of chlorinated compounds. The research focuses on the reactions of pure chlorinated hydrocarbons and oxygen mixtures when exposed to high temperatures in a shock tube. The progress of the reaction is monitored in real time by optical techniques and/or by dynamic pressure measurements. The specific objectives of this study include the following:

1) To use single-pulse shock tube techniques to study the decomposition and formation of products of incomplete combustion during the pyrolysis and oxidation of carbon tetrachloride, methane/carbon tetrachloride mixtures, trichloroethene, and 1,1,1-trichloroethane.
2) To use laser techniques to determine the sooting characteristics of $C_1$ and $C_2$ chlorinated alkanes and alkenes and their mixtures with hydrocarbons during both pyrolysis and rich oxidation.
3) To further kinetic models for combustion ignition delays of selected chlorinated hydrocarbons.

The second area of basic research being conducted within the HWRC involves alternative methods of treatment/destruction. The first project in this area is entitled "Rate Mechanisms in the Supercritical Extraction of Organics from Solid Hazardous Wastes." The principal investigators are F. Carl Knopf, Ed McLaughlin, Robert P. Gambrell, and Kerry M. Dooley.

Supercritical fluid extraction (SCF) of organic hazardous waste from contaminated soils is a promising new technique which could prove particularly useful for hazardous waste site cleanup. In this investigation, supercritical $CO_2$ is used to extract PCBs, DDT, and toxaphene from contaminated topsoils and subsoils. Typically, in SCF extraction a simple solvent gas, such as carbon dioxide, is brought into contact with a solid or liquid phase at high pressure and moderate temperature. The specific objectives of this project are as follows:

1) To construct a SCF extraction unit and develop the technology to aid in the removal of organic hazardous wastes from soil. Such a unit has been constructed and its efficiency is presently being tested on PCB- and DDT-contaminated soils.
2) To study factors that control the rate at which waste is extracted and to try to improve the process on a small pilot plant.

The second Center project in the area of alternate methods of treatment/destruction is entitled "Kinetics and Stability of Genetically Transformed Biodegradative Microbes in Mixed Culture, Mixed Substrate Environments," the principal investigator is Dipak Roy.

In recent years, environmental scientists have isolated a number of microorganisms in the laboratory from natural biota by selective enrichment with specific toxic organic compounds to be biodegraded as the sole source of carbon and energy. This information, while significant in its own right, is limited insofar as its application in the degradation of organics in natural or man-made environments, where a multiplicity of different microbes is involved. The objectives of this study are as follows:

1) To illustrate the growth kinetics and stability of selected bacterial transformants in mixed culture and mixed substrate environments comprised of chlorinated organics and/or toxic heavy metals.
2) To investigate intergenic transfer of plasmids in order to develop bacterial transformants which can biodegrade chlorinated aromatic organics in the presence of heavy metals.

The third area of basic research being pursued at the HWRC is that of Chemicals/Materials Interaction and Stabilization. Two Center projects are presently being funded in this area. The first of these is entitled "Identification of Bonding and Interfering Mechanisms Associated with Stabilized/Solidified Hazardous Organic Wastes." The principal investigators are Marty Tittlebaum, Harvill Eaton, and Frank Cartledge.

A widely used method for disposal of liquid hazardous wastes is solidification/stabilization, in which the liquid is mixed with a suitable second component resulting in a stable, solidified product. While there are several obvious negative aspects associated with this method of treating liquid hazardous wastes, there are arguments which make it a desirable treatment: low cost, straight-forward technology, and a potential for long-term satisfactory performance. The primary objectives of this research effort are as follows:

1) To determine the microscopic distribution of chemical elements and compounds in selected organic hazardous waste/binder systems so that the kinetic behavior of the systems can be described. The organic compounds being used in the study are ethylene glycol and p-bromophenol, and Type I Portland cement is being used as the model binding material.
2) To model the transport of the treated waste as a function of the age of the solidified/stabilized system. This knowledge is significant for two reasons:
   a) It leads to an understanding of whether a particular organic compound is mechanically or chemically bonded.
   b) It could lead to the identification of additives which might more effectively bind wastes over the long term.

The second project in the area of Chemicals/Materials Interaction and Stabilization, is entitled "Activity Coefficients for Hazardous Materials Dissolved In Water." The principal investigator is Frank Groves.

Hazardous materials in the environment will often be found in dilute aqueous solutions in water leachates of sparingly soluble organics from waste dumps or spills, for example. In predicting the transport of such wastes through the environment, it is important to calculate the rate of transfer and equilibrium distribution of the pollutants between the water and the air. The focus of this project is on predictive methods for aqueous solubility, Henry's law coefficients, and octanol-water partition coefficients of sparingly soluble organics based on a knowledge of molecular structure.

The primary objectives are as follows:

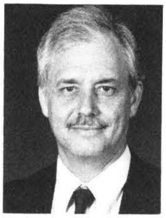
1) To survey the literature and obtain existing data on the aqueous solubility of organic materials, from which the activity coefficients can be readily calculated.
2) To experimentally determine aqueous solubility as a function of temperature and salinity for a small group of sparingly soluble organics.
3) To use data from (1) and (2) to develop an improved UNIFAC group contribution method for estimating activity coefficients.

Since its inception, the Center has been supported primarily by the EPA (through a cooperative agreement). Future funding is contingent upon the success of a new program known as the Industry Associates Program, which is presently in its infancy. Designed to bring about a more active collaboration between industry and the HWRC, the Center is offering industrial organizations the opportunity to share in the findings of HWRC researchers, and to become partners in focusing the direction of the applied research program. The applied research program will be directed by a committee of the scientists/engineers selected from member companies and HWRC researchers. The focus of the program will be long-term generic hazardous waste problems faced by member companies. The funds contributed by Associate membership fees will be used to support additional projects.

The intent of the program is to allow those corporations which do not have adequate resources for independent research (either manpower or dollars) to conduct in-depth research into waste treatment. Even those companies with research facilities may not be able to cope with long-term applied research projects of this magnitude; or they may have their facilities tied up with product improvement or expansion. Since this program would operate much like a mutual fund investment, the cost of research to any one associate would be only a portion of the total cost of doing the work. Yet all of the information generated would be available to each associate in its entirety.

In the four years of its existence, the Center's projects have yielded some rather promising results in the three areas of basic research. With the increased input and support from industry, it is hoped that these results will be put to practical use in solving the hazardous waste disposal/destruction problems which are plaguing the country today.

**Rosalind Segesta** is the Quality Assurance Officer for the Hazardous Waste Research Center at Louisiana State University. Prior to joining the staff at the Center, she was associated with the Louisiana Department of Environmental Quality, where she served as manager of the Water Pollution Control Division's analytical laboratory. She received her Bachelors degree in Chemistry from Louisiana State University, and her Masters in Chemistry from the University of Texas at Austin.



**Louis Thibodeaux** served as Secretary, Treasurer, First Vice Chairman and Chairman of the Environmental Division of AIChE from 1981-85. He received his B.S. in Petroleum Engineering from Louisiana State University, Baton Rouge. Upon graduation, he joined E.I. duPont de Nemours in the Works Technical Department, where his duties included activities in the storage and disposal of radioactive waste. He received a Ph.D. at LSU in Chemical Engineering, specializing in diffusion and mass-transfer. Presently, he is Professor of Chemical Engineering at Louisiana State University and holds an appointment as Director of the LSU EPA-Sponsored Hazardous Waste Research Center. His field of specialization is diffusion and mass-transfer as related to the transport processes of chemicals in the natural environment. He is a Registered Professional Engineer in Arkansas and Louisiana and has served as the principal investigator on nine research projects, authored numerous papers and a textbook entitled CHEMODYNAMICS, plus served as a consultant for several companies.

# Consumption of Pond Water Through Partial Liming: Recent Experience

Charles Wittmann Weston

Agrico Chemical Company, Donaldsonville, LA 70346

*Contaminated, acidic cooling and gypsum pond waters associated with wet-process phosphoric acid production can be treated using a partial liming process. The treatment largely removes the fluoride component, giving a treated water which is suitable for use in the phosphate rock wet grinding circuit; a majority of the phosphate component of the pond water is thereby directly recovered. Although the acidity of the contaminated water is only partially neutralized during treatment, phosphate rock added to the grinding mill contains sufficient carbonate to give a ground rock slurry of low corrosivity. This process has been used successfully during the last four years at Agrico Chemical Company's Faustina Plant to manage occasional water balance problems resulting from high rainfall.*

## INTRODUCTION

Wet-process phosphoric acid plants usually have one, and sometimes two, large ponds containing acidic, contaminated water. One type of pond is associated with the by-product gypsum stack, and thus contains "gypsum pond water." In addition to its use in slurrying and transporting gypsum to stack, this water is often cycled through the plant's barometric condensers, and thus serves as scrubbing and cooling water. However, some plants, such as Agrico Chemical Company's Faustina plant, maintain a separate pond for this latter purpose; circulation of water through this large pond allows it to cool before reuse. Although this water is nominally separate from gypsum pond water, there is always significant, usually purposeful, interchange; thus, the composition of two ponds are often quite similar. Both are acidic (pH 0.9 to 2.1) and contain significant quantities of phosphate, sulfate and fluosilicate ions (See Table 1). Disposal of water of this sort is obviously quite a problem, since it cannot be discharged without treatment.

To avoid discharge, phosphate plants strive to consume as much contaminated water as possible in order to remain in water balance. Gypsum pond water is regularly used as the final wash on the gypsum filter, for example. Unfortunately, in much of the southeastern U.S., annual rainfall, which can reach 165 to 178 centimeters per year, exceeds evaporation. Because rain is the major input to the pond system, plants in the Gulf coastal region are often obliged to treat water for discharge during part of the year. Typical treatment consists of two stage liming using ground limestone and/or slaked lime; contaminants are thus precipitated and removed as insoluble calcium compounds and silica. In addition to the associated operating costs, this sort of treatment results in the permanent loss of previously soluble phosphate in the waste sludge. One answer to this problem for plants which wet-grind phosphate rock would be the use of contaminated pond water instead of fresh water in the grinding circuit. As a result, the $P_2O_5$ in the water would be directly recovered. Additionally, one might suppose that the rock would neutralize a major part of the water's acidity, since most commercial phosphate rocks contains a significant amount of carbonate. However, tests have shown that this is not the case. Even though almost all of the fluoride is removed from solution during grinding, a pond water-ground rock slurry remains quite acidic (pH ≈ 3), and thus corrosive to carbon steel grinding balls and mill liners.

Several alternative ways of dealing with the problem of corrosion/erosion were considered. One of these was constructing a new mill of resistant materials, or rubber lining and sealing the existing mill. However, it was found that commercial carbon steel balls would be consumed at more than twice the normal rate. Several suitably resistant types of alloy balls were found, but their cost was two to four times that of the balls already in use. Thus, this option was eliminated on the basis of cost. Another choice would be the replacement of only part of the fresh water with pond water, but experiments showed that acceptably low corrosion/erosion rates were achieved at only low levels of replacement, viz. below 30%.

TABLE 1. COMPOSITION OF POND WATERS, APRIL, 1984

| Component, mg/l | Cooling Pond | Gypsum Pond |
|---|---|---|
| $P_2O_5$ | 13,850 | 15,390 |
| F | 14,320 | 13,100 |
| $H_2SO_4$ | 9,630 | 10,420 |
| CaO | 1,820 | 1,990 |

A third alternative would involve making use of the above mentioned partial neutralization of the pond water by the rock, and following it by additional neutralization with ammonia or sodium hydroxide. Such processes have been patented and offered for licensing. They do yield near neutral (pH ≈ 6.0) slurries, yet lab tests plus some in-plant experience gave cause to reject this alternative for two reasons:

1. Lab mill tests showed that steel grinding balls still surprisingly suffer relatively high corrosion-erosion rates when exposed to slurry generated by this sort of process.
2. Lab tests, and additionally, inadvertent plant experience, indicated that the use of sodium hydroxide, but especially ammonia, for neutralization would cause significant down-stream problems. Sodium contributes to an already serious scaling problem (as $Na_2SiF_6$) in the phosphoric acid plant piping. Ammonia, on the other hand, causes extensive precipitation, both during and after concentration. It was found that even fairly low levels of ammonium ion contamination of wet-process acid can quickly cause the precipitation of unmanageable quantities of sludge in the 54% $P_2O_5$ acid storage.

## PROCESS DEVELOPMENT

Based upon experience gained in two stage liming, and the development of a process for recovering metallurgical grade fluorspar from cooling pond water, it was realized that the carbonate component of phosphate rock was selectively precipitating insoluble calcium fluoride without causing significant phosphate or sulfate precipitation. Based upon this, it was decided to try to develop a partial liming process. In this process, sufficient fluoride would be removed from the cooling pond water so that the resultant treated water could be safely fed to the phosphoric acid plant wet-grinding circuit. Since it was known that calcium carbonate would ultimately raise the pH of cooling pond water to about 5.4 to 6.0, and that such water was not excessively corrosive, this pH range was chosen as the goal for the final slurry. Within this constraint, it was obviously wished to leave as much $P_2O_5$ in the clarified, treated water as possible.

Figure 1 illustrates the precipitation of fluoride, phosphate and sulfate by addition of finely ground calcium carbonate to cooling pond water; a similar set of curves is obtained when slaked lime is used. For this particular pond water, addition of between 25 and 30 grams per liter $CaCO_3$ effects almost complete precipitation of fluoride, while about 55 to 70% of the $P_2O_5$ remains in solution. The resulting treated water has a pH of 2.5 to 2.9. It was felt that water treated to within this range would be a suitable water feed for the mill.

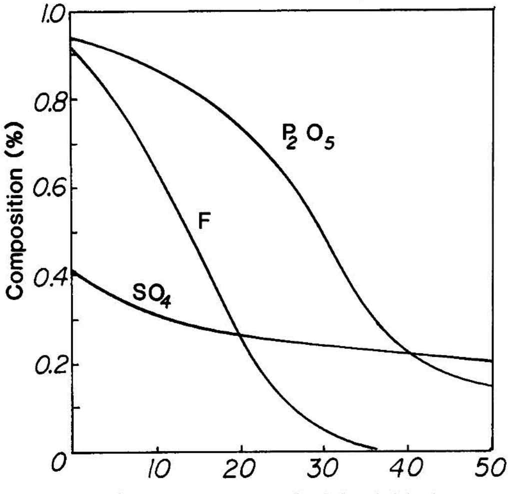


Figure 1. Precipitation of $P_2O_5$, F and $SO_4$ by calcium carbonate.

An extensive series of laboratory scale tests essentially confirmed this conclusion. In these tests, pond water was treated with various levels of calcium carbonate, clarified, and used as feed for a steel, laboratory ball mill. A set of partially eroded balls actually recovered from the plant were used to load the lab mill, along with an appropriate amount of unground rock. Figure 2 gives the starting and final pH's for the 70% solids slurry tested in a grinding cycle. Figure 3 shows the corresponding corrosion-erosion rate for carbon steel mill balls used in these tests. As anticipated, reduction of the soluble fluoride in the partially treated water to about 300 ppm allowed the neutralization of residual phosphoric acid by the carbonate component of the rock to approach completion. This resulted in the formation of a near neutral, relatively non-corrosive ground rock slurry.

Based upon these results, it was decided to carry out a full scale plant test using partially treated pond water. Agrico's Faustina plant mill operates in a closed loop grinding mode; that is, over-sized rock in the slurry leaving the mill is separated in hydrocyclones and returned to the mill. In order to assure maximum contact of the treated water with recycle slurry, the water was added to the cy-

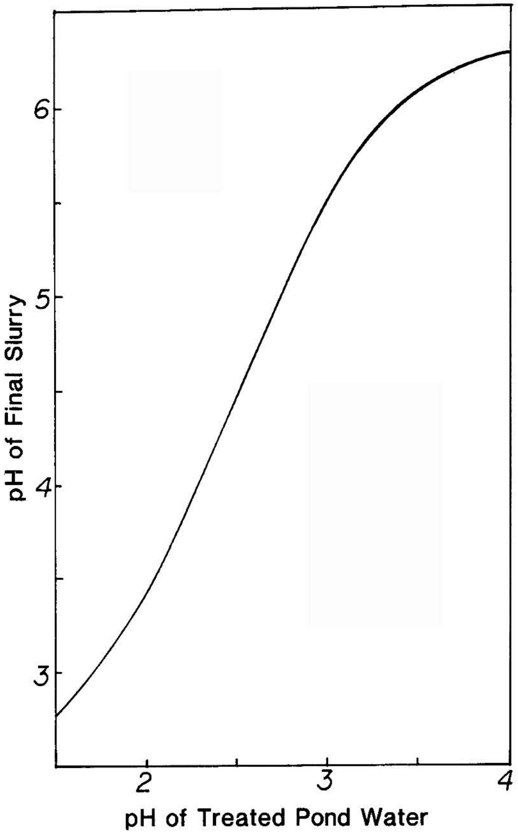


Figure 2. Pilot ball mill test results, pH of final slurry as a function of the pH of treated pond water.

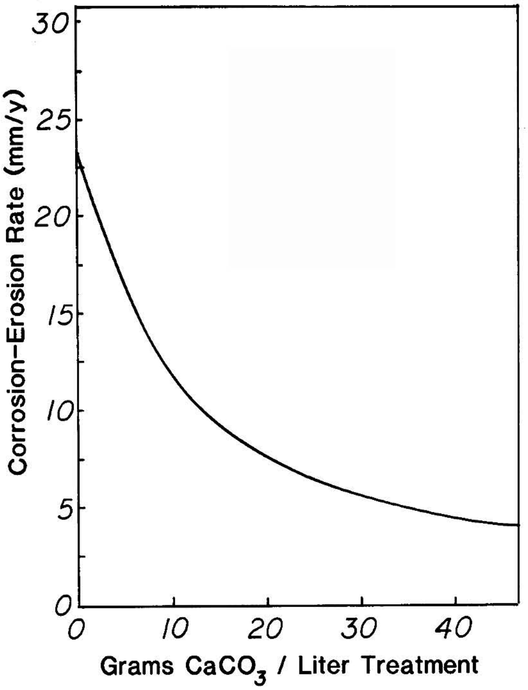


**Figure 3. Corrosion-erosion rate of mill balls versus water treatment level.**

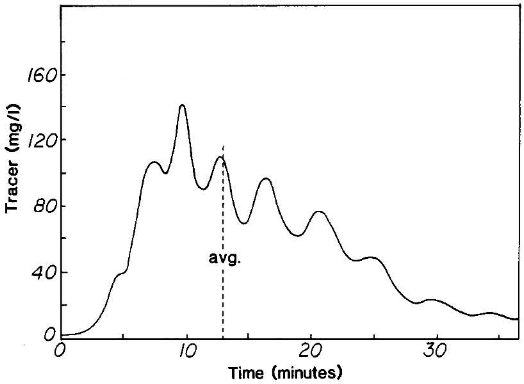


**Figure 4. Ball mill residence time study.**

clone underflow. Earlier work using a tracer while the mill was operating in an open loop mode indicated that the mill had excellent back mixing characteristics (Figure 4).

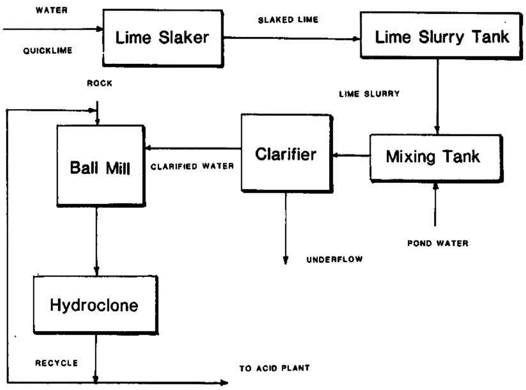


**Figure 5. Flow diagram of the partial liming process.**

Thus, it was not anticipated that there would be a pronounced pH profile through the mill. Consequently, several trials were conducted during January and February of 1982. In these tests, and in all subsequent operation, the cooling pond water was treated in our existing water treatment unit using slaked lime, this being the most economical material (Figure 5). The results showed that pH values of 2.4 to 2.5 must be reached in the water treatment process in order to attain acceptable corrosion protection of the mill; to be prudent, initially 2.6 to 2.8 was chosen as the control range. The results of these tests are shown in Table 2. Note that the mill corrosion rate is indeed just corrosion, since the coupons were positioned such that erosion would be negligible. Also note that the savings listed do not include the cost of treating and discharging water, which up to this time has been budgeted annual at about $900,000 for 370 million liters. At the time these first tests were run, quickline cost was $69 per metric ton.

Since the tests were positive, the process was adopted, and has been used as needed to remain in water balance since 1982. As a result, the Faustina plant has not had to treat and discharge contaminated water, even during the spring of 1983, during which heavy rainfall caused record flooding in the area. Thus, there were no reasons to be concerned with discharge compliance.

Using July through December of 1983 as an example, it can be shown that a total of about 144,000,000 liters of cooling pond water were treated, of this, 136,000,000 liters were consumed in the ball mill. Lime usage averaged 14 kilograms of quicklime per 1000 liters of water for pond water which contained from 10,440 to 11,800 mg/l $P_2O_5$ and from 9,600 to 13,820 mg/l F.

The proportion of $P_2O_5$ recovered in the pond water during this period ranged from 42 to 68% of the input. Average recovery was about 60% the total $P_2O_5$ recycled during this period represents 0.35% of the total $P_2O_5$ produced. If pond water was consumed at the highest pos-

TABLE 2. RESULTS OF 1982 PLANT TEST

| Date | 1/30-2/3 | 2/5-2/8 | 2/10-2/16 | 2/19-2/23 |
|---|---|---|---|---|
| Water Consumed MM Liters | 6.8 | 5.7 | 11.4 | 6.1 |
| Treated Water | | | | |
| pH | 2.8 | 2.78 | 2.55 | 2.62 |
| $P_2O_5$, mg/l | 6640 | 7325 | 8515 | 7980 |
| F, mg/l | 264 | 133 | 122 | 155 |
| Mill Corrosion, MM/Year | 0.38 | 0.69 | 0.79 | 0.58 |
| Slurry pH | 5.5 | 5.4 | 5.3 | 5.3 |
| $P_2O_5$ Recovered* | 1.80 | 1.99 | 2.31 | 2.17 |
| Lime Usage* | 1.43 | 1.43 | 1.43 | 1.43 |
| Net Savings* | 0.37 | 0.56 | 0.88 | 0.74 |

* $/1000 Liters

TABLE 3. COMPOSITION OF POND WATERS, OCTOBER, 1984

| Component, mg/l | Cooling Pond | Gypsum Pond |
|---|---|---|
| $P_2O_5$ | 15,280 | 19,200 |
| F | 17,800 | 13,600 |
| $H_2SO_4$ | 15,950 | 12,870 |
| CaO | 1,640 | 1,710 |

sible rate, this percentage would be about double. However, at Faustina pond water consumption is largely predicated by pond level, all other factors being equal.

Late in 1984, the composition of cooling pond water had changed so that the fluoride content of the water approached 18,000 mg/l, while $P_2O_5$ was about 15,000 mg/l. When this water was treated to a pH of 2.9 in the lime reactor (2.6 in the settling pond), lime consumption increased to over 29 kg/1000 liters; $P_2O_5$ recovery was about 53%. Since gypsum pond water had a higher $P_2O_5$ content, but a lower F content, it was decided to test the treatment of gypsum pond water.

Samples of cooling pond water and gypsum pond water were first studied in our laboratory to define their behavior during lime treatment. The composition of the samples tested is given in Table 3. Figure 6 shows the response of these samples to increasing levels of lime addition. In order to bring the cooling pond water into the target pH range, 31 to 32 grams of CaO per liter were required, while only 24 to 26 grams per liter were needed for gypsum pond water. This 25 to 30 percent increase in lime consumption is primarily associated with the 30% higher fluoride content of the cooling pond water, as illustrated by Figure 7.

The $P_2O_5$ remaining in solution as a function of lime treatment level is shown in Figure 8. At appropriate levels of addition, it was evident that more $P_2O_5$ could be recovered from gypsum pond water than from cooling pond water. Consequently, it was decided that gypsum pond water would be treated instead of cooling pond water. During December of 1984, gypsum pond water averaging 20,800 mg/l $P_2O_5$ and 13,200 mg/l F was treated to an average pH of 2.95 in the lime reactor (equivalent to 2.7 in the settling pond). This treatment dropped the $P_2O_5$ in the treated water to 10,000 mg/l for a 48.5% recovery; average fluoride was about 325 mg/l. During the month, lime usage was 34 kg/1000 liters of water.

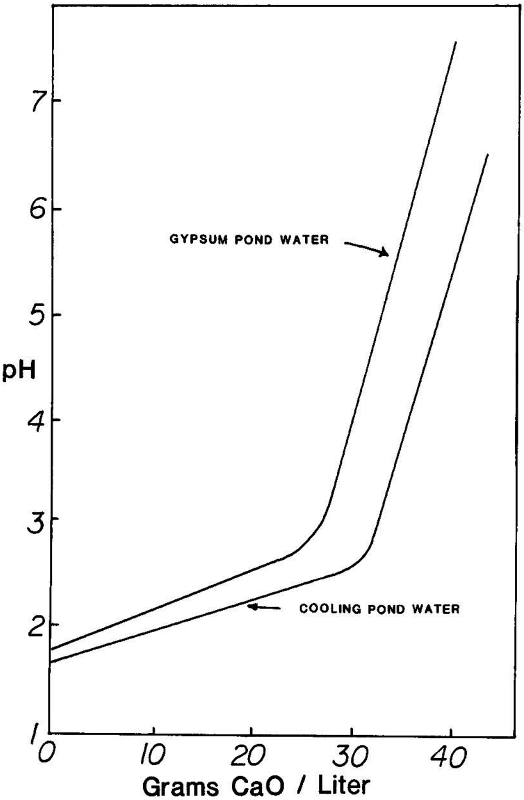


Figure 6. pH of pond waters after various levels of lime treatment.

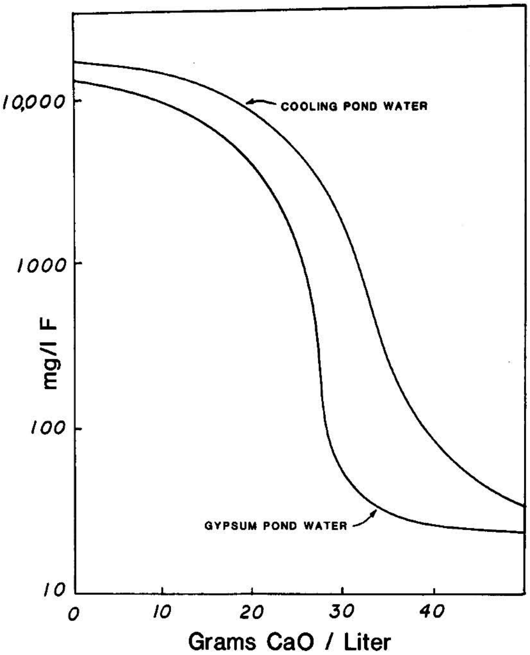


Figure 7. Concentration of residual fluoride in pond waters at various levels of lime treatment.

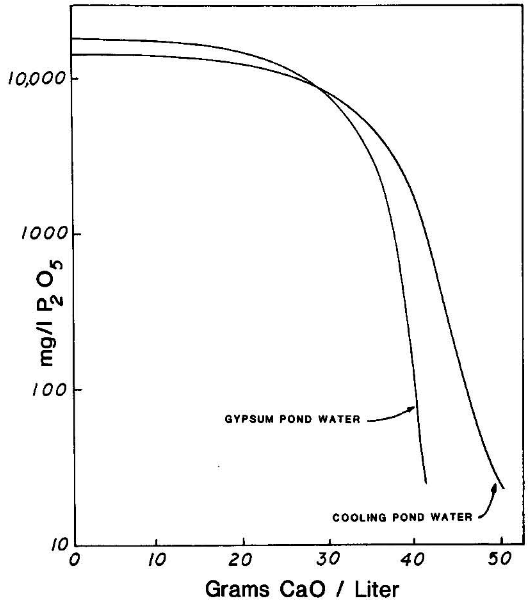
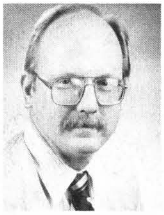


Figure 8. Concentration of residual phosphate as $P_2O_5$ in pond waters at various levels of lime treatment.

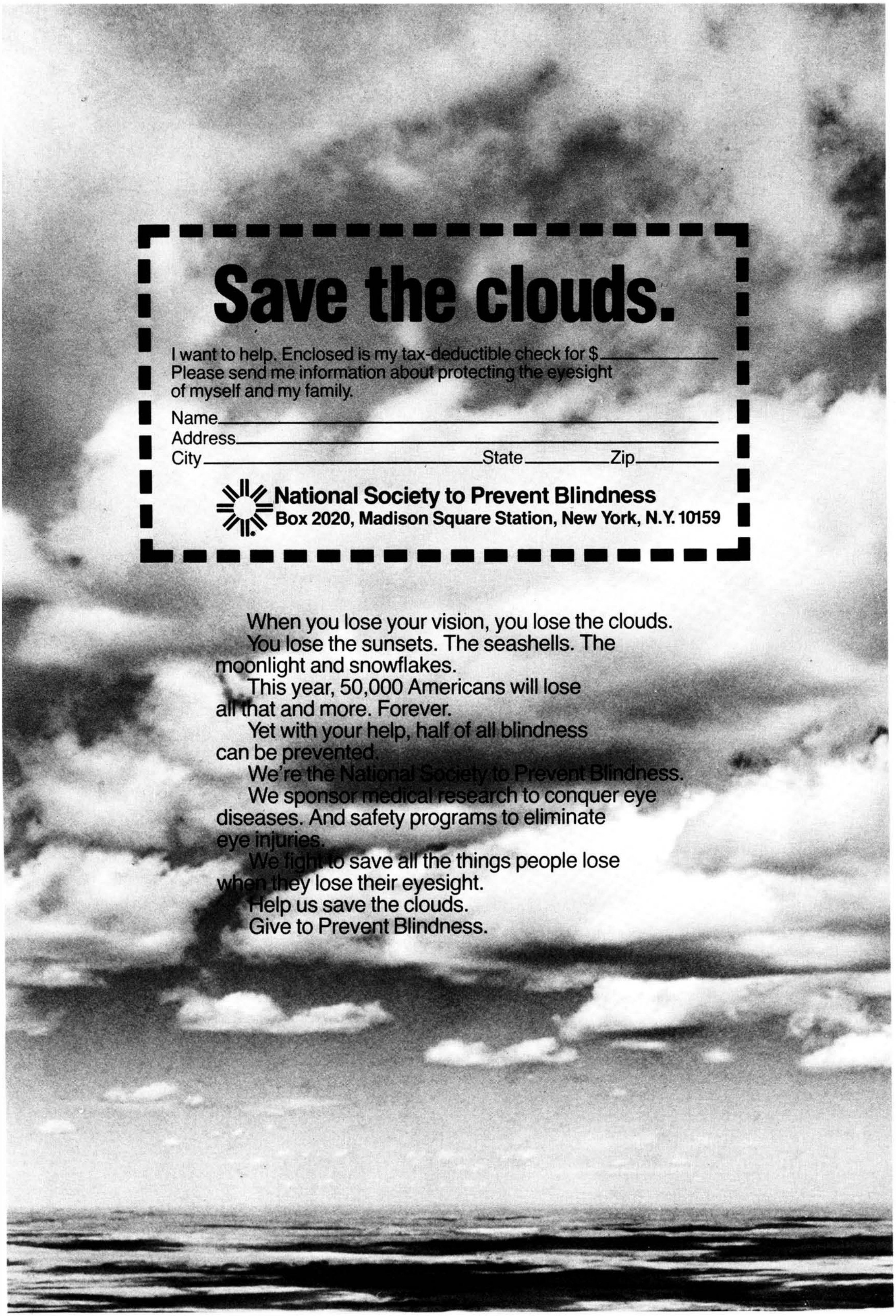
During January, 1985, gypsum pond water averaging 20,500 mg/l $P_2O_5$ and 11,700 mg/l F was treated to a slightly lower pH of 2.8 in the lime reactor (2.45 in the pond). $P_2O_5$ recovery was about 45%, while lime usage dropped to 23 kg/1000 liters of water. Finally, in February, gypsum pond water containing about 19,000 mg/l $P_2O_5$ and 13,000 mg/l F was treated to an average pH of 2.45. Here, $P_2O_5$ recovery increased to about 65%, while lime usage was 25 kg/1000 liters. Treated pond water containing an average of 1.23% $P_2O_5$ was recycled to the ball mill. During this, and the proceeding months, the pH of the ground rock slurry produced in the mill remained in the specified pH range of 5.5 to 6.0.

## CONCLUSION

These results suggest that when treating gypsum pond water to pH values from 2.4 to 2.9, the $P_2O_5$ content of treated water fed to the ball mill will range from about 7,500 to 13,000 mg/l. However, since gypsum pond water will have a high initial $P_2O_5$ content, the actual proportion of $P_2O_5$ recovered will be somewhat low unless the treatment pH is held in the lower part of the safe range. Thus, experience using heavily contaminated gypsum pond water instead of cooling pond water illustrates the effect of both relative and absolute impurity content and treatment pH on $P_2O_5$ recovery and lime consumption.



**Charles W. Weston** is Manager of Research and Development for Agrico Chemical Company. He received a B.S. in chemistry from Mississippi State University in 1966, and a Ph.D. from Tulane University in 1970. He is a member of the American Association for the Advancement of Science, the New York Academy of Science, and is presently Chairman of the Division of Fertilizer and Soil Chemistry of the American Chemical Society.



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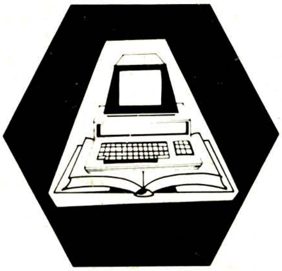

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